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The system was evaluated in sampling trips to Los Angeles, Niagara Falls, and Houston. The results for the analyses for the 20 selected compounds as well as additional broad-scan data are presented.

Analyses of the samples were accomplished using thermal desorption of the sorbent materials followed by capillary column gas chromatography/mass spectrometry (GC/MS). A sample collected in Houston was also analyzed using a multi-detector capillary column GC system having a conventional flame ionization detector, a N-P flame ionization detector, a photoionization detector and an electron capture detector. A comparison of the GC/MS and multidetector GC results was made.

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ABSTRACT

A sampling system was developed for collecting 20 significant probable or possible atmospheric carcinogens from ambient air. The sampling system is based on a combination of solid sorbent materials consisting of Tenax-GC, Porapak R, and Ambersorb XE-340 arranged in series. Air samples are drawn through this system using a Nutech Model 221-1A pump.

The system was evaluated in sampling trips to Los Angeles, Niagara Falls, and Houston. The results for the analyses for the 20 selected compounds as well as additional broad-scan data are presented.

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SECTION 1

INTRODUCTION

The general population, particularly in urban areas, is exposed to a wide variety of atmospheric pollutants. The health hazard posed by this situation cannot currently be adequately defined because of the complexity of the problem and the lack of sufficient, reliable data. One of the needs in assessing this exposure problem is a reliable screening technique for determining what substances at what concentrations are present in our ambient atmosphere. Although the U.S. Environmental Protection Agency has a concern for a wide range of pollutants that appear in our environment, those materials that are carcinogenic pose a special concern owing to their potentially adverse health effects.

The ability to assess the extent of a carcinogen hazard in ambient air requires at least three things:

(1) Knowledge of the materials that pose the hazard,

(2) A reliable sampling technique for collecting these materials, and

(3) Adequate technology for accurate analyses of these materials.

These three requirements provided direction for the major thrusts of this research program. A group of 20 significant probable or possible atmospheric carcinogens was selected, and the sampling and analytical technologies were developed/acquired to assess their presence/concentrations in urban environments.

The result of this research is a sampling system and associated analytical methodology that is capable of screening for a broad range of organic components in ambient air and in particular for assessing the presence/absence of the selected 20 potential carcinogenic compounds. This represents the first step toward a reliable approach for assessing the health hazard associated with carcinogenic materials in ambient air.

SECTION 2

CONCLUSIONS

A three-sorbent sample collection system was designed, evaluated, and field tested in Los Angeles, Niagara Falls, and Houston. The sorbents were operated in series drawing air in turn through Tenax GC, Porapak R and Ambersorb XE-340 using a Nutech Model 221-1A pump. This selection of sorbent materials was judged the best combination of commercially available sorbents for broad-range organics sampling.

The sampling system operated as anticipated in field sampling applications. The need for additional, complimentary sorbent capabilities to those of Tenax was demonstrated in the Los Angeles and Houston samples where significant amounts of organics were observed on the subsequent (Porapak and Ambersorb) tubes. A partial fractionation was also observed on the various sorbent materials where different ranges of compounds (based primarily on volatility) were found. There appears to be some influence exerted by matrix and/or humidity effects on the amount of breakthrough that is observed on the latter sorbents. The Niagara Falls samples were collected in an interior environment and exhibited little if any compound breakthrough to the Porapak and Ambersorb materials.

The number of compounds from the target list of 20 probable or possible carcinogens observed in actual field samples was small. The largest number and highest concentrations were observed in the Niagara Falls samples.

The analytical methodology was based primarily on capillary column GC/MS using thermal desorption for recovering the sample from the sorbents for analysis. Samples collected in high humidity environments (e.g., Houston) caused particular problems in the analysis phase due to high concentrations of water collected on the Porapak and Ambersorb sorbents. However, it was found that by changing certain analytical parameters (e.g., initial GC temperature), a satisfactory analysis could be performed in these instances. One sample set from Houston was also analyzed using a multi-detector capillary GC technique. The results showed that the multi-detector approach offered advantages over conventional GC in terms of selectivity and specificity. However, it cannot replace GC/MS for unequivocal identification of compounds. This approach might more appropriately be applied to assessment of compound types as a more general indicator of overall air quality.

SECTION 3

RECOMMENDATIONS

The following recommendations are made as the result of the research conducted on this program:

(1) The sampling system that was developed should be extensively evaluated in other field sampling situations to further define its operational capabilities.

(2) The technique should be used primarily as a "screen" for the presence/absence of specific compounds or for wide-scan evaluation of organic composition in ambient air much as the EPA Priority Pollutant Protocol is used as a "screen" for organics in industrial effluents.

(3) Only after the system has been validated for a specific compound(s) in a particular air matrix should it be used to generate quantitative data.

(4) Validation should consist of the use of spikes to determine actual recoveries of the compounds of interest. Stable isotopically labelled compounds should be used where possible to allow differentiation between the spike and the native compound.

(5) When a compound of concern is identified through the screening process, careful consideration and confirming studies should be made to determine if this compound is real or an artifact of the sampling/analytical techniques.

(6) The multi-detector GC approach should be further evaluated to determine its value. This would include development of computer assisted data reduction techniques to draw together the vast amount of information that is generated and to compare the responses from the various detectors.

SECTION 4

PROGRAM OVERVIEW

OBJECTIVE

The objective of this research program was to develop sampling and analytical techniques for twenty of the most significant potentially carcinogenic atmospheric pollutants and to demonstrate the developed technology in field tests in selected urban areas.

PROGRAM

The program that was developed to address this objective was divided into three phases that roughly paralleled the three years of the contract (outlined in Figure 1). Phase 1 dealt with the background study and selection of compounds for consideration in this program. The Phase 1 activities developed a basis for prioritizing atmospheric pollutants and enabled the selection of the 20 compounds to be studied in this program. In addition, a review of the carcinogen cofactor literature was conducted, and isopleths for potential sampling sites were generated using the MRC Source Assessment Data Base and the EPA Climatological Dispersion Model. The results from these first three activities of Phase 1 were reported in a separate report [1]. The final activity of Phase 1, a review of sampling and analysis techniques for chemical classes, was completed and appears as Appendix A of this report.

The second phase of the program dealt with the selection and laboratory testing of a broad-range sampling system based on commercially available sorbent materials and the associated methodology needed to complete the analysis of the collected samples. This phase had much in common with a companion program

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[1] McMillin, C. R., L. B. Mote, and D. G. DeAngelis. Potential Atmospheric Carcinogens, Phase 1: Identification and Classification. EPA-600/2-80-015, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1980. 253 pp.

Phase 1

- Select 20 significant atmospheric carcinogens
- Review carcinogenic cofactors
- Generate carcinogen isopleths for year 3 sampling sites
- Review sampling and analysis techniques for chemical classes

Phase 2

- Develop polypollutant sampling systems using several polymer sorbents
- Develop analytical procedure

Phase 3

- Field test sampling and analysis methodology in selected cities
- Evaluate multi-detector capillary GC analysis
- Deliver test system to EPA

Figure 1. Program outline for EPA Contract No. 68-02-2773.

(EPA Contract No. 68-02-2774) aimed at the development of a portable collection system for carcinogens in ambient air. The related contract included research on the selection and evaluation of candidate sorbent materials, and the development of rationale for the final combination of materials for use in a portable sampling system. Capillary GC/MS techniques were evaluated for use as the "analytical finish" to the sampling system. The results from these studies are contained in Sections 5-8 of this report.

The final phase of the program involved the field evaluation of the system in actual sampling applications. Samples were collected in Los Angeles, Niagara Falls, and Houston using the sampling system developed on this program. The results from the sampling and subsequent analyses are discussed in Sections 9-10.

An additional study involving the evaluation of a multi-detector capillary GC system for the analysis of the samples was conducted in conjunction with the Houston sampling trip. This study was a first attempt to evaluate the possibility of using GC with various selective and non-selective detectors as an alternative to GC/MS for the analysis of complex environmental samples. The results from this study are discussed in Section 11.

SECTION 5

REVIEW OF SAMPLING AND ANALYTICAL TECHNIQUES AND COMPILATION OF PERTINENT DATA

OBJECTIVE

A literature review of existing sampling and analytical techniques was to be conducted which emphasized methods that could be used for developing a means of quantitatively determining selected, potentially carcinogenic, atmospheric pollutants.

INSTRUMENTATION

Information on exisiting sampling and analytical techniques for organic atmospheric pollutants and sampling applications for the twenty selected compounds was obtained by using MRC's Information Retrieval System. The system provided access to bibliographic citations in 240 data bases through a Texas Instrument's Inc., Silent 700 electronic data terminal. By entering carefully selected combinations of key words, bibliographies were obtained of journal articles, government reports, patents, books, and on-going research projects pertaining to the subjects of interest. Citations of particular interest were noted. Complete copies of these citations (articles, books, etc.) were obtained from MRC's technical library.

REVIEW

Sampling and Analysis Techniques

An extensive literature search was conducted which surveyed the existing sampling and analysis methods and techniques for organic materials including the potential carcinogens of interest. This review is given in Appendix A of this report.

Compilation of Pertinent Data

In addition to this extensive review, a brief literature survey of the twenty, selected potential carcinogens was also conducted (in part under EPA Contract No. 68-02-2774). The purpose of this study was to acquire information on these compounds for practical laboratory use concerning:

- Pertinent physical properties (Table 1),
- Hazards and proper handling practices (Table 2),
- Mass spectral characteristics (Table 3), and
- Environmental and occupational sampling applications.

In addition to basic properties and handling procedures for these compounds, insight was sought into the problems and potential problems associated with sampling and analyzing these potential carcinogens.

The literature on sampling applications was obtained using MRC's Information Retrieval System (previously described), while information on physical characteristics, hazardous properties, and mass spectra was obtained from common reference materials. Most of the literature on sampling applications discussed specific sampling and analytical procedures for one or a few compounds, usually in ambient or workplace air. A few references gave a review of previous literature and an overview of techniques available for a specific compound. A few others evaluated methodologies used in laboratory validations, statistical treatments of data, laboratory handling of hazardous chemicals, and relevant sampling programs. Basic research into sorbent characteristics, sampling phenomena, etc., were also discussed in a few references. A directory of the information available in these articles is given in Table 4. The values reported in these references for the concentrations of various compounds found in air samples are compiled in Table 5.

DISCUSSION

The literature review of existing sampling and analytical techniques, and sampling applications revealed that a wide variety of techniques and methods are available for obtaining and evaluating air samples. Unfortunately, many of these sampling and analytical techniques are not applicable to the simultaneous determination of compounds varying widely in volatility and functionality. For example, glass filters can be used to obtain high-volume particulate samples containing organic compounds such as benzo(a)pyrene. Volatile compounds such as carbon tetrachloride, however, are not collected by this technique.

For this project the sampling technique determined to be the most applicable to the collection of the twenty selected compounds was adsorption on solid sorbent materials. More specifically, this project was to address the use of a combination of solid sorbents, complimentary in their adsorption characteristics, such that the compounds of interest could be collected using a single sampling system.

TABLE 1. PERTINENT INFORMATION FOR THE SELECTED COMPOUNDS

Compound information [2]				Physical properties [2]				
Name	Synonyms	Structure	CAS. No. [5]	M.W., g/mol	Den, g/mL	M.P., °C	B.P., °C	Vap. P., Pa (mm Hg)
1. Acrolein	Acrylaldehyde, propenal, acrylic aldehyde	$CH_2=CHCHO$	107-02-8	56.06	0.841	-87.7	52.5	2.9×10^4, (220) @20°C
2. Acrylonitrile	Propenenitrile, vinyl cyanide	$CH_2=CHCN$	107-13-1	53.06	0.797 0.806	-82	78-9	1.3×10^4, (100) @23°C
3. Benzene	Benzol, benzole, phene	C_6H_6	71-43-2	78.11	0.879	5.5	80.1	1.0×10^4, (76) @20°C
4. Benzidine	p,p'-bianiline, 4,4'-diaminobiphenyl	$NH_2C_6H_4$-$C_6H_4NH_2$	92-87-5	184.2	1.250	116-130	401.7 subl	--
5. Benzo(a)pyrene	1,4-benzopyrene	$C_{20}H_{12}$	50-32-8	252.3	--	177	312^{a} 1.3×10^3 Pa, (10 mm Hg)	--
6. Benzyl chloride	α-chlorotoluene	C_6H_5-CH_2Cl	100-44-7	126.6	1.103	-43	179	130, (1) @22°C
7. Carbon tetrachloride	Tetrachloromethane	CCl_4	56-23-5	153.8	1.595	-23	76.8	1.2×10^4, (90) @20°C
8. Chrysene	Benzo(a)phenanthrene	$C_{18}H_{12}$	218-01-9	228.3	--	255-6	448	--
Cumene hydroperoxide	Dimethylbenzylhydroperoxide	C_6H_5-$C(CH_3)_2$-OOH	80-15-9	~152	--	--	153	130, (1) @70°C
9. Di-(2-ethylhexyl) phthalate (DEHP)	Dioctyl phthalate (DOP)	C_6H_4-$[CO_2CH_2$-$(C_2H_5)C_4H_9]_2$	117-81-7	390.6	0.986	-55	385	160, (1.2) @200°C
10. 1,4-Dioxane	(1,4) diethylene dioxide, glycol ethylene ether	$OC_2H_4OC_2H_4$	123-91-1	88.12	1.034	11.8	101	4.0×10^3, (30) @20°C
11. Ethylene dichloride	1,2-dichloroethane	$ClCH_2CH_2Cl$	107-06-2	96.96	1.257	-35.4	83.5	8.1×10^3, (61) @20°C
12. Ethylene oxide	1,2-epoxyethane, oxirane	CH_2CH_2O	75-21-8	44.05	0.882	-111	10.7	1.5×10^5, (1095) @20°C
13. Hexachloro-1,3-butadiene	--	$CCl_2=CCl$-$CCl=CCl_2$	87-68-3	260.8	1.682	-21	215	2.9×10^3, (22) @100°C
14. Pentachlorophenol	--	Cl_5C_6OH	87-86-5	266.4	1.978	191	310 decom	1.4×10^{-2}, (1.1×10^{-4}) @20°C
15. Styrene	Vinyl benzene, phenyl ethylene, cinnamate	$C_6H_5CH=CH_2$	100-42-5	104.16	0.907	31	146	670, (5) @20°C
16. Tetrachloroethylene	Perchloroethylene	$CCl_2=CCl_2$	127-18-4	165.83	1.505	-22.4	121.0	1.9×10^3, (14) @20°C
Tetraethyl lead	--	$Pb(C_2H_5)_4$	78-00-2	323.5	1.659	--	198.2	20, (0.15) @20°C
17. Toluene-2,4-diamine	4,m-tolylenediamine, 2,4-diaminotoluene, 2,4-toluylenediamine	$CH_3C_6H_3(NH_2)_2$	95-80-7	122.2	--	99	280	130, (1) @106.5°C
18. Vinyl acetate	Acetic acid, ethenyl ester	$CH_3CO_2CH=CH_2$	108-05-4	86.09	0.932	-93.2	72.2	1.1×10^4 (83) @20°C
19. Ethylene dibromide	1,2-dibromomethane	$Br_2CH_2CH_2Br$	106-93-4	187.9	2.170	9.8	131.4	--
20. 1,3-Dichloropropene	(cis) (trans)	$ClCH_2CH=CHCl$	542-75-6	111.0 111.0	1.473 1.468	-- --	104.3 112	-- --

(continued)

TABLE 1 (continued)

		Solubility parameter [3,4]				Pollutant information [1]			
		δ Calc[a] [3]	Calc Sm[b]	Lit Sm[b]	δ Lit[a] [4]	Carcinogen	Emissions, kg[c]	Half life, da	Priority,[d] kg
1.	Acrolein	10.0	560	--	--	Possible	1.1×10^4	0.11	6.4×10^1
2.	Acrylonitrile	10.8	573	557	10.5	Probable	3.7×10^6	--	1.7×10^2
3.	Benzene	9.2	719	719	9.2	Probable	5.9×10^7	3	3.4×10^5
4.	Benzidine	--	--	--	--	Probable	3.5×10^4	1	4.8×10^1
5.	Benzo(a)pyrene	--	--	--	--	Probable	8.3×10^5	--	8.3×10^5
6.	Benzyl chloride	9.9	1253	--	--	Probable	4.1×10^5	--	3.4×10^2
7.	Carbon tetrachloride	9.4	1447	1323	8.6	Probable	1.6×10^7	70-230	9.3×10^4
8.	Chrysene	--	--	--	--	Probable	1.7×10^4	--	6.1×10^2
	Cumene hydroperoxide	--	--	--	--	Possible	8.2×10^4	<0.2	4.8×10^2
9.	Di-(2-ethylhexyl) phthalate (DEHP)	--	--	--	--	Possible	1.2×10^6	1	7.0×10^3
10.	1,4-Dioxane	10.9	956	881	9.9	Probable	1.3×10^6	0.40	7.5×10^3
11.	Ethylene dichloride	10.4	1013	--	--	Probable	9.1×10^7	10-1000	1.1×10^5
12.	Ethylene oxide	15.0	660	489	11.1	Possible	3.8×10^4	0.13	2.2×10^2
13.	Hexachloro-1,3-butadiene	10.4	2783	--	--	Possible	3.4×10^6	<1	2.0×10^4
14.	Pentachlorophenol	--	--	--	--	Possible	2.1×10^7	>72	5.4×10^4
15.	Styrene	9.0	940	969	9.3	Possible	5.6×10^6	--	3.2×10^4
16.	Tetrachloroethylene	10.6	1758	1542	9.3	Probable	8.5×10^7	2-8	4.9×10^5
	Tetraethyl lead	--	--	--	--	Possible	4.7×10^6	2-3	3.4×10^4
17.	Toluene-2,4-diamine	--	--	--	--	Probable	4.4×10^5	--	5.3×10^3
18.	Vinyl acetate	8.9	769	--	--	Possible	6.8×10^5	--	2.2×10^3
19.	Ethylene dibromide	10.9	2053	--	--	Probable	2.1×10^6	<0.83	2.0×10^4
20.	1,3-Dichloropropene	11.9 11.6	1318 1314	-- --	-- --	Possible	2.2×10^7	3	7.3×10^4

[a] $(2.045\ J^{1/2})/cm^3$.

[b] $(2.045\ g\ J^{1/2})/(cm^3 \bullet mol)$.

[c] Emissions, kg = source emissions, kg/yr (365 da) x half life, 1 da.

[d] Priority, kg = emissions, kg x average mutagenic potency relative to benzo(a)pyrene.

KEY

CAS No. - Chemical Abstract Service Number	Vap. P. - Vapor Pressure
M.W. - Molecular Weight	calc - Calculated
Den. - Density	lit - Literature
M.P. - Melting Point	subl - Sublimes
B.P. - Boiling Point	decom - Decomposes

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[3] Small, P. A. Some Factors Affecting the Solubility of Polymers. Journal of Applied Chemistry, 3(2):71-90, 1953.

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[5] Chemical Abstracts, Ninth Collective Index, Formulas. ISSN:0097-6474. Library of Congress Cat. No. 9-4698. American Chemical Society, Chemical Abstracts Services, Columbus, Ohio, 1978.

TABLE 2. HAZARDOUS PROPERTIES OF SELECTED COMPOUNDS

			Sax hazard information (6)												
						Disaster			Health hazard ratings						
	Flash point, °C(°F)	TLV, ppm	Fire						Acute local				Acute syst		
Compound			Heat	Flame	Expl	Rx wi oxid	Toxic fume	Expl (Rx)	Irr	All	Ing	Inh	Ing	Inh	SAb
1. Acrolein	<-18 (<0)	0.01	V Dang	V Dang	V Dang	V Dang			3	1	3	3	3	3	2
2. Acrylonitrile	-1 (30)	20	Dang	Dang		Dang							Highly toxic		
3. Benzene	-11 (12)		Dang	Dang		Dang			2		1	1	2	2	2
4. Benzidine							Dang		U	U	U	U	3	3	3
5. Benz(a)pyrene															
6. Benzyl chloride	67 (153)	1	Mod	Mod		Dang		Mod	3		3	3	3	3	3
7. Carbon tetrachloride	none	10					Dang		0	0	0	0	3	3	1
8. Chrysene															
Cumene hydroperoxide	79 (175)		Mod	Mod				Dang	3		3	3	3	3	3
9. Di-(2-ethylhexyl) phthalate (DEHP)	218 (425)		Slt	Slt					0	0	1	1			
10. 1,4-Dioxane	12 (54)	90	Dang	Dang		Dang			2				3	3	3
11. Ethylene dichloride	13 (56)	50	Dang	Dang		Dang	?		3				3	3	
12. Ethylene oxide	<-18 (<0)	50	SVR	SVR	SVR	SVR		SVR	3					2	
13. Hexachloro-1,3-butadiene							?								
14. Pentachlorophenol							Dang		3				3	3	2
15. Styrene	31 (88)	100	Dang	Mod		Dang			2				2	2	
16. Tetrachloroethylene	none	100					Dang		2				3	2	2
Tetraethyl lead			Mod	Mod		Dang							Highly toxic		
17. Toluene-2,4-diamine			V	V		V	Mod		2				2	2	
18. Vinyl acetate	-8 (18)	10	Dang	Dang		Dang			1				1		
19. Ethylene dibromide	none	20						Dang	3	3			3	3	3
20. 1,3-Dichloropropene	35 (95)		Mod	Mod		Dang	?		2		2	2	2	-	-

(continued)

TABLE 2 (continued)

	Sax hazard information [6]					Patty hazard information [7]				
	Health hazard ratings									
	Chr loc		Chr syst			Flash point, °C(°F)	Auto ig temperature, °C(°F)	TLV, ppm	Oral LD_{50}, mg/kg	
Compound	Irr	All	Ing	Inh	SAb					General description
1. Acrolein	3	1	U	U	U	<-18 (<0)			66	Irritant, highly toxic; flammable.
2. Acrylonitrile		Highly toxic				-3 (27)	482 (900)	20	35-90	Irritant, highly toxic; flammable.
3. Benzene	0	0	3	3	3	-11 (12)		25		Toxic, flammable.
4. Benzidine	U	U	3	3	3					Extremely toxic and carcinogenic.
5. Benzo(a)pyrene										Toxic and carcinogenic.
6. Benzyl chloride	U	U	U	U	U					Irritant, rxts with oxidizers, toxic.
7. Carbon tetrachloride	1		3	3	3	none	none	10	2,920	Toxic.
8. Chrysene										Toxic and carcinogenic.
Cumene hydroperoxide	U	U	U	U	U					Irritant, toxic, oxidizer rxts violently
9. Di-(2-ethylhexyl) phthalate (DEHP)	0	0	2	2	1	218 (425)			24,000 35,000	Low toxicity-plasticizer.
10. 1,4-Dioxane	U	U	3	3	2	18 (65)		100	3,000 6,000	Toxic, irritant; flammable.
11. Ethylene dichloride	2		3	3	2	18 (65)	413 (775)	100	680	Very toxic irritant; flammable.
12. Ethylene oxide	2				U	-20 (-4)		50	100-100	Very toxic, irritant, highly flammable; rxts with oxidizers; explosion hazard.
13. Hexachloro-1,3-butadiene										Toxic and carcinogenic.
14. Pentachlorophenol			2	2	2			0.046	20-200	Highly toxic, irritant.
15. Styrene	U	U	2	2	-	30 (86)		100		Irritant, toxic; mod, flammable.
16. Tetrachloroethylene	2		2	2	2	none		100		Anesthetic; toxic.
Tetraethyl lead		Extremely toxic								Extremely toxic.
17. Toluene-2,4-diamine	U	U	2	2						Toxic.
18. Vinyl acetate	1		U	U	U	-22 (8)			2,900	Flammable; toxic.
19. Ethylene dibromide	2		2	2	2	none		25	60-500	Highly toxic irritant.
20. 1,3-Dichloropropene	U	U	U	U	U					Irritant; flammable; toxic.

HEALTH HAZARD RATINGS

0 - None
1 - Slight
2 - Moderate
3 - High
U - Unknown

KEY

Acute syst - Acute systemic
All - Allergen
Auto ig - Autoignition
Chr loc - Chronic local
Chr syst - Chronic systemic
Dang - Dangerous
Expl - Explosion
Expl (Rx) - Explosion by reaction
Ing - Ingestion
Inh - Inhalation
Irr - Irritant
Mod - Moderate
Rx wi oxid - Reacts with oxides
SAb - Skin Absorption
Slt - Slight
SVR - Severe
Temp - Temperature
V Dang - Very Dangerous

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[7] Patty, F. A., ed. Industrial Hygiene and Toxicology, 2nd Ed., Vol. II. Interscience Publishers, New York, New York, 1962.

TABLE 3. MASS SPECTRAL INFORMATION FOR SELECTED COMPOUNDS [8]

Compound	Molecular weight, g/mol	Emperical formula	Eight major MS peaks [m/z ratio (relative intensity)]							
			1	2	3	4	5	6	7	8
Acrolein	56	C_3H_4O	27 (100)	56 (83)	25 (70)	55 (64)	28 (51)	26 (49)	29 (43)	18 (31)
			27 (100)	56 (65)	26 (59)	28 (53)	55 (44)	29 (39)	25 (9)	14 (4)
			27 (100)	56 (70)	28 (60)	26 (53)	55 (49)	29 (40)	25 (8)	53 (5)
			27 (100)	56 (74)	28 (66)	26 (54)	55 (53)	29 (37)	25 (8)	38 (5)
			27 (100)	26 (57)	56 (55)	28 (48)	29 (44)	55 (39)	31 (8)	37 (7)
Acrylonitrile	53	C_3H_3N	26 (100)	53 (99)	52 (75)	51 (32)	27 (18)	25 (10)	50 (8)	38 (7)
			26 (100)	53 (92)	52 (75)	51 (33)	27 (23)	25 (11)	38 (10)	50 (8)
			53 (100)	52 (73)	26 (70)	51 (28)	28 (10)	27 (9)	50 (7)	25 (4)
			53 (100)	26 (93)	52 (79)	51 (30)	27 (12)	50 (7)	25 (5)	54 (5)
			26 (100)	53 (96)	52 (73)	51 (32)	27 (22)	28 (13)	25 (12)	38 (9)
			53 (100)	26 (70)	52 (69)	51 (27)	27 (10)	50 (7)	25 (4)	54 (3)
			53 (100)	26 (97)	52 (75)	28 (41)	51 (36)	27 (23)	25 (10)	50 (10)
Benzene	78	C_6H_6	78 (100)	77 (19)	51 (19)	52 (17)	50 (14)	39 (12)	79 (9)	76 (6)
			78 (100)	52 (19)	51 (18)	50 (16)	77 (14)	39 (13)	79 (6)	76 (6)
			78 (100)	52 (18)	77 (17)	51 (16)	50 (13)	39 (10)	79 (5)	74 (5)
			78 (100)	51 (21)	52 (20)	50 (18)	39 (14)	77 (14)	79 (7)	38 (6)
			78 (100)	52 (18)	51 (17)	77 (15)	50 (14)	39 (11)	79 (7)	76 (5)
			78 (100)	52 (19)	77 (18)	51 (16)	39 (13)	50 (13)	79 (7)	76 (6)
			78 (100)	77 (19)	52 (15)	51 (13)	50 (10)	39 (9)	79 (6)	74 (4)
			78 (100)	77 (24)	52 (18)	51 (15)	39 (12)	50 (12)	79 (7)	75 (5)
			78 (100)	77 (19)	52 (15)	51 (13)	39 (10)	50 (9)	79 (7)	76 (5)
			78 (100)	77 (19)	52 (16)	51 (15)	50 (11)	39 (10)	79 (6)	76 (5)
			78 (100)	52 (25)	77 (23)	51 (16)	50 (15)	79 (10)	74 (5)	76 (4)
Benzidine	184	$C_{12}H_{12}N_2$	184 (100)	92 (15)	183 (12)	185 (12)	156 (6)	167 (5)	182 (4)	166 (4)
			184 (100)	185 (15)	183 (11)	92 (8)	36 (7)	156 (4)	182 (4)	167 (4)
Benzo(a)pyrene	252	$C_{20}H_{12}$	252 (100)	126 (23)	253 (21)	250 (16)	125 (15)	113 (9)	112 (7)	126 (7)
Benzyl chloride	126	C_7H_7Cl	91 (100)	126 (28)	128 (9)	65 (9)	92 (8)	63 (6)	39 (5)	89 (5)
			91 (100)	126 (23)	2 (15)	19 (13)	65 (12)	63 (10)	92 (9)	128 (7)
			91 (100)	126 (22)	92 (16)	63 (12)	39 (6)	128 (5)	28 (5)	45 (5)
			91 (100)	126 (28)	65 (9)	92 (8)	63 (6)	89 (5)	39 (5)	125 (4)
Carbon tetrachloride	152	CCl_4	117 (100)	119 (99)	121 (34)	82 (22)	46 (20)	84 (15)	35 (14)	36 (12)
			117 (100)	119 (96)	121 (32)	82 (24)	47 (21)	84 (15)	35 (11)	49 (7)
			117 (100)	119 (97)	121 (32)	82 (19)	47 (13)	84 (13)	35 (6)	49 (4)
			117 (100)	119 (96)	47 (48)	35 (44)	82 (30)	121 (30)	84 (19)	49 (15)
Chrysene	228	$C_{18}H_{12}$	228 (100)	226 (20)	229 (19)	114 (15)	113 (13)	44 (10)	101 (7)	227 (6)
			228 (100)	226 (25)	229 (20)	113 (18)	114 (17)	101 (10)	227 (9)	100 (8)
			228 (100)	226 (22)	229 (19)	114 (16)	113 (14)	101 (9)	227 (7)	100 (6)
Cumene hydroperoxide	152	$C_9H_{12}O_2$	43 (100)	119 (91)	105 (76)	121 (74)	77 (67)	91 (43)	120 (33)	51 (30)
			43 (100)	105 (77)	121 (43)	77 (42)	51 (26)	120 (19)	78 (13)	39 (11)

(continued)

TABLE 3 (continued)

Compound	Molecular weight, g/mol	Emperical formula	Eight major MS peaks [m/s ratio (relative intensity)]							
			1	2	3	4	5	6	7	8
Di-(2-ethylhexyl) phthalate	390	$C_{24}H_{38}O_4$	149 (100)	57 (72)	43 (48)	41 (42)	54 (39)	167 (38)	70 (30)	55 (28)
			149 (100)	279 (51)	167 (39)	57 (32)	70 (26)	71 (21)	55 (19)	123 (17)
			149 (100)	279 (64)	167 (46)	57 (16)	113 (14)	114 (14)	156 (14)	280 (14)
			149 (100)	57 (73)	43 (50)	41 (50)	105 (44)	167 (42)	74 (37)	56 (17)
			149 (100)	57 (37)	167 (27)	43 (27)	70 (23)	71 (23)	41 (22)	55 (17)
			149 (100)	57 (54)	169 (33)	71 (27)	70 (27)	43 (20)	55 (19)	113 (14)
			57 (100)	44 (99)	55 (79)	41 (65)	70 (60)	43 (46)	72 (45)	56 (28)
			149 (100)	57 (48)	43 (28)	71 (24)	41 (20)	55 (18)	279 (17)	167 (16)
1,4-Dioxane	88	$C_4H_8O_2$	28 (100)	29 (37)	88 (31)	58 (24)	15 (17)	31 (17)	27 (15)	30 (13)
			28 (100)	88 (53)	58 (40)	29 (28)	31 (16)	30 (15)	43 (12)	15 (11)
			28 (100)	88 (36)	58 (32)	29 (27)	31 (16)	30 (14)	15 (11)	43 (10)
			28 (100)	88 (54)	58 (44)	29 (32)	43 (17)	27 (11)	57 (11)	30 (11)
			28 (100)	58 (68)	29 (54)	31 (31)	43 (27)	27 (24)	30 (24)	57 (19)
			28 (100)	29 (32)	58 (24)	88 (22)	31 (16)	27 (15)	30 (13)	41 (11)
Ethylene dichloride	98	$C_2H_4Cl_2$	62 (100)	27 (70)	49 (50)	64 (33)	63 (27)	98 (23)	51 (17)	61 (16)
			62 (100)	27 (86)	49 (37)	64 (32)	26 (29)	63 (17)	51 (11)	61 (11)
			62 (100)	27 (91)	49 (40)	64 (32)	26 (31)	63 (19)	98 (14)	51 (13)
Ethylene oxide	44	C_2H_4O	29 (100)	44 (79)	15 (55)	43 (23)	14 (21)	42 (17)	28 (9)	16 (8)
			44 (100)	29 (98)	15 (50)	43 (23)	42 (15)	14 (13)	16 (6)	28 (4)
			29 (100)	15 (65)	44 (65)	14 (26)	43 (16)	26 (14)	42 (12)	13 (8)
			44 (100)	29 (83)	15 (53)	43 (22)	42 (13)	14 (12)	15 (3)	45 (3)
Hexachloro-1,3-butadiene	258	C_4Cl_6	225 (100)	227 (65)	223 (63)	190 (43)	260 (36)	188 (32)	118 (30)	141 (29)
			225 (100)	227 (64)	223 (63)	260 (43)	190 (39)	262 (34)	188 (30)	141 (26)
Pentachlorophenol	264	C_6HOCl_5	266 (100)	268 (70)	264 (68)	165 (54)	167 (52)	95 (44)	130 (30)	60 (28)
			266 (100)	268 (65)	264 (63)	165 (29)	36 (29)	167 (28)	270 (23)	230 (18)
Styrene	104	C_8H_8	104 (100)	103 (38)	78 (31)	51 (30)	77 (20)	50 (15)	39 (11)	52 (11)
			104 (100)	102 (69)	51 (45)	103 (39)	78 (24)	39 (23)	50 (19)	52 (16)
			104 (100)	103 (45)	78 (32)	51 (21)	77 (17)	105 (9)	50 (7)	52 (7)
			104 (100)	103 (38)	78 (27)	51 (25)	77 (17)	50 (9)	52 (9)	105 (9)
Tetrachloro-ethylene	164	C_2Cl_4	166 (100)	164 (78)	129 (64)	131 (62)	168 (48)	94 (21)	133 (20)	96 (14)
			166 (100)	164 (79)	129 (69)	131 (66)	168 (48)	47 (42)	94 (40)	35 (35)
			166 (100)	164 (79)	129 (61)	131 (58)	168 (46)	94 (28)	133 (19)	96 (18)
Toluene-2,4-diamine	122	$C_7H_{10}N_2$	121 (100)	122 (15)	94 (10)	105 (8)	104 (8)	77 (5)	61 (5)	123 (4)
Vinyl acetate	86	$C_4H_6O_2$	43 (100)	15 (15)	28 (10)	27 (8)	42 (8)	86 (5)	44 (5)	14 (4)
			43 (100)	15 (9)	86 (9)	27 (6)	42 (5)	44 (4)	28 (4)	29 (2)
			43 (100)	45 (26)	28 (25)	60 (14)	29 (14)	42 (13)	44 (13)	27 (6)
			43 (100)	15 (13)	86 (6)	27 (6)	42 (5)	44 (5)	28 (3)	14 (3)
Ethylene dibromide	186	$C_2H_4Br_2$	107 (100)	109 (95)	27 (54)	28 (11)	26 (8)	93 (5)	188 (5)	95 (4)
			27 (100)	107 (77)	109 (72)	26 (24)	28 (10)	79 (5)	25 (5)	93 (4)
1,3-Dichloropropene	110	$C_3H_4Cl_2$	75 (100)	39 (55)	77 (32)	49 (26)	110 (20)	38 (14)	112 (13)	36 (10)
			75 (100)	77 (33)	39 (33)	110 (25)	49 (17)	112 (16)	38 (6)	51 (6)

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[8] Eight Peak Index of Mass Spectra, 2nd ed., Vol. I. Mass Spectrometry Data Centre, Aldermaston, Reading, U.K., 1974.

TABLE 4. DIRECTORY OF INFORMATION CONTAINED IN LITERATURE REFERENCES

	References																																			
Information	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Compounds																																					
Acrolein			P[a]	all pertain																all pertain	x												all pertain				x
Acrylonitrile		P	P											x				x				x					x										
Benzene		x	x		x	x	P				x			x				x									x			x							
Benzidine			P					P?																													
Benzo(a)pyrene	x							x					x				x								x	x		x	P					x			
Benzyl chloride		x	P		P							x																									
Carbon tetrachloride		P	x		x	P	P							x													x	P		x		x			x		
Chrysene	P							x					P				x								P	P		x	P					P			
Cumene hydroperoxide																																					
Di-(2-ethylhexyl)phthalate			x					x							x	x		P																			
Dioxane		x	P							x																				x							
Ethylene dichloride		P	P		P	P	P							x													x	P		x		P			x		
Ethylene oxide		x	x			x			x					x																							
Hexachloro-1,3-butadiene			P					P							P?	P?							x														
Pentachlorophenol		P	P					x							P?	P?																				P	
Styrene		P	x		P	x	x					P						x						x													
Tetrachloroethylene		P	x		x	x	P							x													x	P		P		x			x		
Tetramethyl lead																			x												x						
Toluene-2,4-diamine																																					
Vinyl acetate		P	P				P																				x										P
Ethylene dibromide		P	P		P	P	P							x													x	P		P		P			P		
1,3-Dichloropropene		P	P		P	P	P							x													x	P		P		P			P		
Sampling:																																					
Type of Sample																																					
Ambient Air	x	x	x			x		x					x		x	x	x		x				x		x	x			x		x	x	x	x			
Workplace Air	x	x	x				x		x	x	x	x			x			x		x	x	x	x	x			x	x		x			x		x	x	
Other Air	x		x										x	x									x										x				x
Water (only)					x																																
Method of Sampling																																					
Solid Sorbent			x		x	x	x	x		x	x	x			x	x		x	x	x	x		x	x			x	x		x		x	x		x	x	x
Type[b]			var[c]		Tx	Tx	AC	Tx		AC	AC	Tx			Fal	Fal		Fal, SG, AC	var	var	AC		Tx	AC			AC	AC		AC		PoN	var		AC	AC	Tx
Other[d]	F	B	var					F	I				F				F		F	F		D	F		F	F		F	F					F			
Particulate Assoc.	x							x					x				x		x	x			x		x	x		x	x		x			x			
Analysis:																																					
Description (S,T)[e]	S		S&T		T	T	S	S		S	S	T	S		S	S	S	S		S	S		S	S	S	S		S	S	S		T	S&T	S	S	S	T
Solvent[f]	cyh		var				CS_2	Bz, MeOH		CS_2	CS_2		cyh		pet eth, et eth	pet eth, et eth		MeOH, CS_2, et acc		var	et DiCl		hex	CS_2	Bz	Cyh		CS_2 Cyh	Bz	CS_2				?	CS_2	et eth	
Temp (°C)																																200					350
Resolution[g]	GC		var		CGC	CGC	GC	GC	GC	GC	GC	GC	HPLC		GC	GC		GC	var	GC	GC		GC	GC	TLC	GC		GC& CC	CC& TLC	GC		GC		TLC	GC	GC	GC
Detection[h]	Fl	IR	var		MS	MS	FID	MS		FID	FID	MS	Fl&UV		EC	EC		FID &MS	var	AA& FID	FID	IR	EC	FID	Fl	Fl	FID	FID &UV	UV-Vis &Fl	FID		Fl& MS		Fl	MS	FID	FID
Results																																					
Quantitative	x		x		x	x	x	x	x	x		x	x		x	x		x	x		x	x	x	x		x		x	x	x		x	x	x	x	x	x
Qualitative		x						x											x			x			x												
General Information:																																					
Safety				x							x			x			x		x	x							x		x	x	x		x		x		
Previous Lit.				x																x																	
Mutagenicity											x								x												x						
Sampling Data														x															x	x							
Basic Research																	x										x			x			x		x		

[a] P - this article pertains to this compound since similar compounds are utilized.

[b] Type of Sorbent
AC - Activated charcoal
Fal - Florisil
PoN - Porapak N
SG - Silica Gel
Tx - Tenax GC

[c] var - various

[d] Other sampling methods
B - Bag (usu. Tedlar)
D - Direct sample
I - Impinger
F - Filter

[e] S - solvent; T - thermal

[f] Solvents
Bz - benzene
CS_2 - carbon disulfide
chy - cyclohexane
et ace - ethyl acetate
et DiCl - ethylene dichloride
et eth - ethyl ether
hex - hexane
MeOH - methanol
pet eth - petroleum ether

[g] Resolution technique
CC - Column chromatography
CGC - Capillary gas chrom
GC - Gas chromatography
HPLC - High performance
TLC - Thin layer chrom.

[h] Detection technique
AA - Atomic adsorption
EC - Electron capture
Fl - Fluorescence
FID - Flame ionization det.
IR - Infrared spec.
MS - Mass spec.
UV - Ultra-violet spec.
Vis - Visible spec.

See references on the following pages.

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TABLE 5. CONCENTRATIONS OF VARIOUS COMPOUNDS IN AIR SAMPLES REPORTED IN LITERATURE REFERENCES

Compound	Concentration	Reference	Type of air sample
Benzene	1.3-15 ppb[a]	11	Ambient
	1.3-15 ppb	14	Ambient
Benzo(a)pyrene	(with B(e)P & perylene)		
	8 - 40 ng/m^3	16	Ambient
	1 - 3 ng/m^3	21	Ambient
	200 - 300 ng/m^3	21	Downwind from coke oven
	0.1 - 2.0 ng/m^3	25	Los Angeles, CA
	0.122 - 1.76 ng/m^3	34	Urban areas
	ND - 57 ng/m^3	36	Rubber factory (outside)
	0.003 - 1.98 ng/m^3	42	Charleston, SC
Carbon tetrachloride	30 - 130 ppt	40	Ambient
Chrysene	[with B(a)A]		
	5 - 30 ng/m^3	16	Ambient
	0.2 - 2.0 ng/m^3	25	Los Angeles, CA
DDT	0.002 - 0.09 ng/m^3	24	Over open ocean
Dibutyl phthalate	0.08 - 2.5 ng/m^3	24	Over open ocean
Di-(2-ethylhexyl) phthalate	(phthalate ester)		
	>10 mg/m^3	11	Car interior
	126 - 200 ng/m^3	16	Ambient
	30 - 70 ng/m^3	23	Office area
	0.4 - 3,370 ng/m^3	27	Ambient (various)
Pentachlorophenol	1 - 3 ng/m^3	16	Ambient
Perchloroethylene (tetrachloroethylene)	30 - 130 ppt	40	Ambient
Polychlorinated biphenyls (PCB)	35 - 90 ng/m^3	23	Office area
	0.1 - 1.0 ng/m^3	24	Over open ocean

[a] Information in both references provided by the same authors.

The analytical technique determined to be most suitable for the determination of the twenty compounds was gas chromatography combined with mass spectroscopy (GC/MS). Gas chromatography has been used in various applications for all twenty of the compounds of interest. Mass spectroscopy is also widely applicable and aids in compound identification/confirmation by producing mass spectra for compounds eluting from a chromatograph.

To further aid in compound identification by retention time data, maximum gas chromatographic resolution, through the use of capillary columns, was desired. As an alternative to mass spectrometric detection, simultaneous detection by three to five different, general and selective, gas chromatographic detectors (e.g., flame ionization, electron capture, photoionization, etc.) was also to be quickly evaluated.

The technique of compound desorption, thermal or solvent, from the sorbent materials prior to GC/MS analysis was to be determined experimentally. The greater sensitivity attainable by thermal desorption was to be evaluated in comparison to the greater compound stability and (frequently, though not necessary) more reproducible desorption efficiencies attainable by solvent desorption.

The literature survey of the twenty, selected, potential carcinogens indicated significant difficulties associated with the sampling of two compounds in particular, tetraethyl lead and cumene hydroperoxide. Tetraethyl lead was found to be an extremely toxic compound which to obtain required an on-site inspection of laboratory facilities by its supplier. In addition, it was indicated to be a relatively unstable compound that readily thermally degrades and that may not persist in the atmosphere [19, 31] as a pollutant. Cumene hydroperoxide was found to be a very strong oxidizing agent which also would not likely persist in the atmosphere due to its extreme reactivity. Such a reactive compound was thought to present a particular problem with potential *in-situ* reactions when concentrated in a sorbent cartridge. Therefore, these two compounds, tetraethyl lead and cumene hydroperoxide, were replaced as compounds of interest by two alternate compounds, ethylene dibromide and 1,3-dichloropropene (cis and trans isomers).

A few general problems were found to be associated with the twenty selected compounds. For example, highly volatile compounds could not be quantitatively retained on solid sorbents if the sampling volume was very high; while non-volatile compounds, such as benzo(a)pyrene, which exist in the atmosphere at concentrations lower than volatile compounds, generally could not be detected analytically without very high sampling volumes. Another problem was that reactive compounds, such as styrene and ethylene oxide, which tend to polymerize on active surfaces, were more effectively retained on sorbents which had relatively more active surfaces. These paradoxes indicated areas where compromises would be required to obtain a single sampling system.

SECTION 6

SELECTION OF SORBENT MATERIALS

OBJECTIVE

Based on the review of sampling and analytical techniques, the sampling technique determined to be the most applicable to the collection of the twenty selected compounds was sampling with a system containing an appropriate combination of solid sorbents. Sorbent materials having complimentary adsorption characteristics were to be selected so that all twenty compounds could be collected for subsequent analysis with a system using these sorbents.

EVALUATION

The selection of sorbent materials to be incorporated into a sampling system for this contract was largely based on work previously performed for EPA Contract 68-02-2774. Under this contract a combination of sorbent materials was to be selected for use in a portable collection system. Ideally, these sorbents also were to have complimentary adsorption characteristics so that this portable sampling system could collect compounds varying widely in volatility, polarity, and functionality.

Before beginning studies to evaluate and select sorbent materials for EPA Contract 68-02-2774, a comprehensive review of available literature on the use of solid sorbent materials for sampling organic vapors was conducted. Information was collected on specific sampling applications for over 110 compounds using more than 30 different sorbent materials [46]. The pertinent knowledge obtained from this review included:

- Capacity/efficiency information for various compounds on various sorbents,
- A variety of desorption techniques, thermal and solvent,

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[46] Brooks, J.J., and D. S. West. Solid Sorbent Digest. Monsanto Research Corporation, Environmental Analytical Sciences Center, Dayton, Ohio, 1978. 126 pp.

- General knowledge of sorbent properties, capabilities, and problems, and
- Possible experimental techniques for sorbent evaluation and sampling validation.

Six sorbent materials were selected for further laboratory characterizations. These sorbents were Tenax-GC, Porapak R, Porapak N, Chromosorb 104, Ambersorb XE-340, and SKC Inc. activated charcoal (which is used in NIOSH tubes). Later, Chromosorb 104 was eliminated from consideration and laboratory evaluations.

A matrix of test compounds representing a wide variety of polarities, volatilities, and functionalities, was selected for laboratory characterizations of the sorbent materials. This matrix of aliphatic and aromatic compounds is presented in Table 6.

TABLE 6. ALIPHATIC AND AROMATIC TEST COMPOUND MATRIX

	Polarity		
	Hydrocarbons	Halogenated compounds, aldehydes, ethers, ketones and esters	Nitro compounds, nitriles, amines, and strong acids, alcohols and phosphates
Volatility	Low	Medium	High
Low	n-Hexadecane Phenanthrene	Hexachloro-1,3-butadiene 4-Bromodiphenylether	Succinonitrile o-Nitroaniline
Medium	iso-Octane Naphthalene	bis-(2-Chloroethyl) ether 1,2,4-Trichlorobenzene	Ethylene glycol Nitroanisole
High	n-Butane Benzene	Propylene oxide Benzyl chloride	Acrylonitrile Phenol

The sorbent materials (Tenax-GC, Porapak R, Porapak N, Ambersorb XE-340, and SKC Inc. activated charcoal) were then evaluated in the laboratory for their abilities to collect the compounds in the test matrix and low molecular weight aliphatics. A gas chromatographic technique involving the generation of Arrhenius plots was used to estimate sorbent capacities. With chromatographic columns packed with the sorbents of interest, the test matrix compounds were analyzed at various temperatures. By plotting the elution volume per gram of sorbent versus the reciprocal of the absolute temperature (Arrhenius plot) elution volumes could be extrapolated to room temperature (20°C). This provides a estimate of the volume of air which could be drawn through a sorbent tube containing a given amount of sorbent before a test compound would begin to elute or "break through". The data obtained from these experiments are compiled in Table 7.

TABLE 7. COMPILATION OF CAPACITY AND SOLUBILITY PARAMETER DATA

Name	δ_m [4], lit	δ_m [3], calc	MW	Tenax-GC		Porapak R		Porapak N		Ambersorb XE-340		SFC Charcoal	
				$^{FET}Vg_{20°C'}$ L/g	log ^{FET}Vg	$^{FET}Vg_{20°C'}$ L/g	log ^{FET}Vg	$^{FET}Vg_{20°C'}$ L/g	log ^{FET}Vg	$^{FET}Vg_{20°C'}$ L/g	log ^{FET}Vg	$^{FET}Vg_{20°C'}$ L/g	log ^{FET}Vg
Methane	89	-	16.04	-	-	-	-	-	-	0.009	-2.046	0.047	-1.328
Ethane	180	-	30.07	-	-	-	-	-	-	0.229	-0.640	2.40	0.380
Propane	282	282	44.09	-	-	-	-	-	-	5.33	0.727	162	2.210
n-Butane	395	401	58.12	0.16	-0.800	4.93	0.693	3.9	0.591	106	2.025	12 x 10^3	4.079
n-Pentane	505	519	72.15	-	-	-	-	-	-	7,500	3.875	2 x 10^5	5.301
Propylene oxide	534	-	58.08	3.14	0.497	12.4	1.092	17.6	1.246	-	-	-	-
Acrylonitrile	557	573	53.06	9.35	0.971	16.8	1.225	69	1.839	-	-	-	-
n-Hexane	629	638	86.17	-	-	-	-	-	-	4 x 10^5	5.602	-	-
Benzene	719	719	78.11	82	1.914	175	2.244	239	2.378	-	-	-	-
iso-Octane	788	834	114.22	0.532	-0.274	1.550	1.550	2,900	3.462	-	-	-	-
Ethylene glycol	906	-	62.07	120	2.070	-	-	-	-	-	-	-	-
Succinonitrile	-	1,073	80.09	1.04 x 10^4	4.015	-	-	-	-	-	-	-	-
Phenol	1,176	-	94.11	5,460	3.737	-	-	3 x 10^{12} [a]	12.477 [a]	-	-	-	-
Benzyl chloride [b]	-	1,253	126.58	1.02 x 10^4	4.007	-	-	6.6 x 10^5	5.820	-	-	-	-
Naphthalene	1,269	1,410	128.16	3,260	3.513	-	-	-	-	-	-	-	-
Bis(2-chloroethyl) ether [b]	1,402	1,402	143.02	1.06 x 10^4	4.025	-	-	2.8 x 10^6	6.443	-	-	-	-
o-Nitroaniline	-	1,657	138.12	2.9 x 10^4	4.460	-	-	-	-	-		-	-
m-Nitroanisole	-	1,684	153.13	1.14 x 10^4	4.058	-	-	-	-	-	-	-	-
Phenanthrene	1,747	-	178.22	1.9 x 10^6	6.282	-	-	-	-	-	-	-	-
n-Hexadecane	1,811	1,766	226.43	1.3 x 10^5	5.113	-	-	-	-	-	-	-	-
1,2,4-Trichlorobenzene [b]	-	2,014	181.46	1.57 x 10^4	4.195	-	-	-	-	-	-	-	-
4-Bromodiphenyl ether [b]	-	2,616	249.11	2.4 x 10^6	6.377	-	-	-	-	-	-	-	-
Hexachloro-1,3-butadiene [b]	-	2,783	267.6	1.15 x 10^4	4.059	-	-	-	-	-	-	-	-

[a] Potentially large experimental error.

[b] Halogenated.

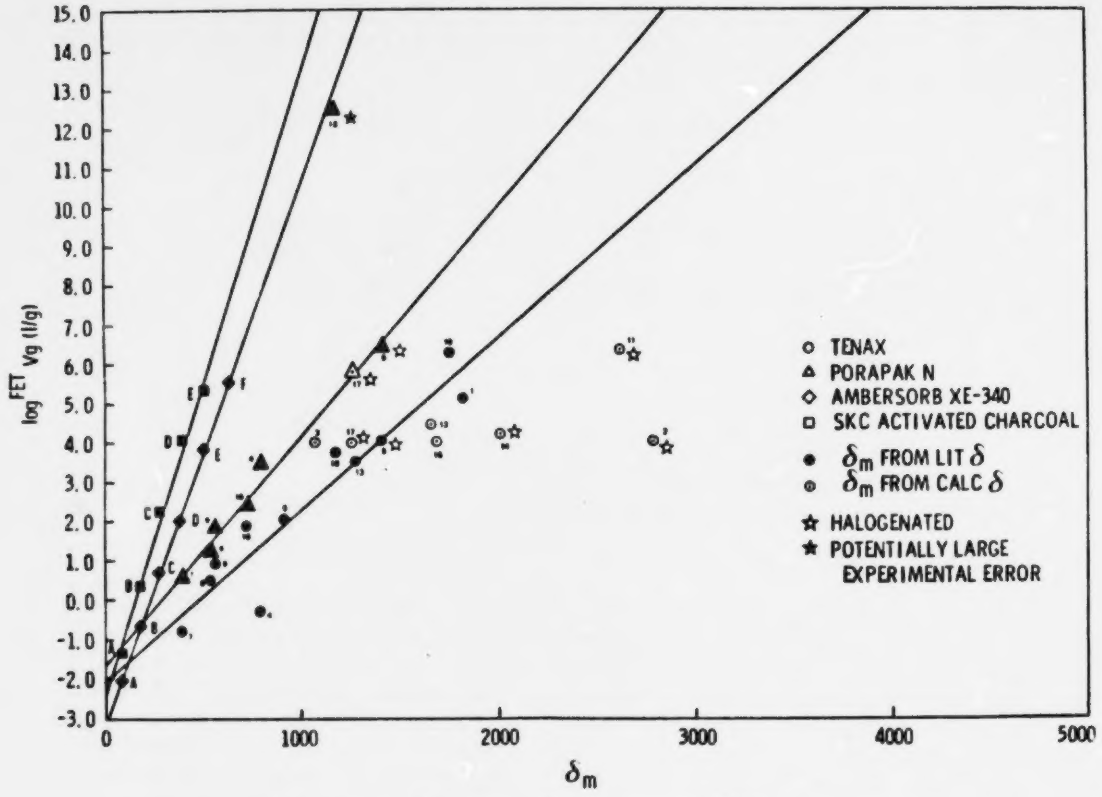
A means of correlating sorbent capacities with compound properties was sought such that a sorbent's ability to collect any given compound would be estimated (based on the properties of that compound). A molecular weight-modified solubility parameter (δ_m), a value combining compound properties of intermolecular forces of attraction and molecular weight was found to give reasonable correlation with the sorbent capacity data experimentally obtained. This is demonstrated by Table 8 and Figure 2.

TABLE 8. CORRELATION COEFFICIENTS FOR δ_m VERSUS LOG $^{FET}Vg_{20°C}$

Sorbent material	Correlation coefficient
SKC charcoal	0.996
Ambersorb XE-340	0.999
Porapak N	0.993
Porapak R	0.944
Tenax-GC	0.806
Tenax-GC (excluding halogenated compounds)	0.916

A number of experiments were also conducted to determine how amenable the selected sorbents were to thermal desorption of the test matrix compounds. These desorption properties were very quickly evaluated by desorbing standard solutions of the test matrix compound through small sorbent-filled tubes into a gas chromatograph. Compounds having small elution volumes at high chromatograph temperatures during sorbent capacity determination were found to be efficiently desorbed. The ability of sorbents to efficiently desorb collected compounds also was found to favorably correlate with a compound's solubility parameter. A qualitative comparison of δ_m with sorbent capacity and desorption efficiency is given in Table 9. The enclosed regions indicate compounds which are probably or possibly quantitatively collected and are probably or possibly quantitatively desorbed from the sorbent materials indicated (assuming a sample volume of 480L and 1 g of sorbent). These regions correspond to ranges of δ_m values listed in Table 10.

Other areas of laboratory evaluation of the sorbent materials included an investigation of conditioning and handling procedures, level and composition of sorbent background, and pressure drops across various sorbent tube designs packed with the sorbent materials. Table 11 summarizes the major results of the sorbent characterization (conducted under EPA Contract 68-02-2774).



Fi

KEY	Name	Key	Name
A	Methane	18	Phenol
B	Ethane	17	Benzyl chloride
C	Propane	13	Naphthalene
D(7)	n-Butane	5	Bis-(2-chloroethyl) ether
E	n-Pentane	12	*o*-Nitroaniline
8	Propylene oxide	15	*m*-Nitroanisole
9	Acrylonitrile	10	Phenanthrene
F	n-Hexane	1	n-Hexadecane
16	Benzene	14	1,2,4-Trichlorobenzene
4	iso-Octane	11	4-Bromodiphenyl ether
6	Ethylene glycol	2	Hexachloro-1,3-butadiene
3	Succinonitrile		

Figure 2. Correlation of δ_m and log $^{FET}Vg_{20°C}$ for test compounds on sorbent materials.

TABLE 9. QUALITATIVE EVALUATION OF TWO SORBENT PROPERTIES COMPARED TO δ_m TO DETERMINE RANGES OF SORBENT UTILITY

Name	δ_m[4], lit	δ_m[3], calc	Tenax-GC Trap	Tenax-GC Desorb	Porapak R Trap	Porapak R Desorb	Porapak N Trap	Porapak N Desorb	Ambersorb Trap	Ambersorb Desorb	SKC Charcoal Trap	SKC Charcoal Desorb
Methane	89	-	00	!	00	!	00	!	00	!	00	!
Ethane	180	-	00	!	00	!	00	!	00	!	00	!
Propane	282	282	00	!	00	!	00	!	00	!	00	!
n-Butane	395	401	00	!	00	!	00	!	00	!	✓	!?
n-Pentane	505	519	00	!	00	!	00	!	✓	!?	✓	!?
Propylene oxide	534	-	00	!	00	!	00	!	✓	!?	✓	!?
Acrylonitrile	557	573	00	!	00	!	00	!	✓	!?	✓	!?
n-Hexane	629	638	00	!	00	!	00	!	✓	!?	✓	X
Benzene	719	719	00	!	00	!	00	!	✓	!?	✓	X
iso-Octane	788	834	00	!	✓	!	✓	!	✓	X	✓	X
Ethylene glycol	906	-	00	!	✓	!	✓	!	✓	X	✓	X
Succinonitrile	-	1,073	✓	!	✓	!	✓	!	✓	X	✓	X
Phenol	1,176	-	✓	!	✓	!?	✓	!?	✓	X	✓	X
Benzyl chloride	-	1,253	✓	!	✓	!?	✓	!?	✓	X	✓	X
Naphthalene	1,269	1,410	✓	!	✓	!?	✓	!?	✓	X	✓	X
Bis(2-chloroethyl) ether	1,402	1,402	✓	!	✓	!?	✓	!?	✓	X	✓	X
o-Nitroaniline	-	1,657	✓	!	✓	X	✓	X	✓	X	✓	X
m-Nitroanisole	-	1,684	✓	!	✓	X	✓	X	✓	X	✓	X
Phenanthrene	1,747	-	✓	!	✓	X	✓	X	✓	X	✓	X
n-Hexadecane	1,811	1,766	✓	!	✓	X	✓	X	✓	X	✓	X
1,2,4-Trichlorobenzene	-	2,014	✓	!	✓	X	✓	X	✓	X	✓	X
4-Bromodiphenyl ether	-	2,616	✓	!	✓	X	✓	X	✓	X	✓	X
Hexachloro-1,3-butadiene	-	2,783	✓	!	✓	X	✓	X	✓	X	✓	X

KEY

	Probably	Possibly	Not Likely
Trap Quantitatively	✓	✓?	00 (Vg <480 ℓ/g)
Desorb Quantitatively	!	!?	X

TABLE 10. RANGES OF UTILITY OF SOLID SORBENTS BASED ON δ_m

Sorbent	δ_m (Trap)	to	δ_m (Desorb)
SKC charcoal	∿350	to	∿600
Ambersorb	∿450	to	∿750
Porapak N	∿750	to	∿1,500
Porapak R	∿750	to	∿1,500
Tenax-GC	∿950	to	>2,800

A more detailed discussion of these evaluations is available in the literature [47].

RESULTS

Of the five sorbent materials evaluated for EPA contract 68-02-2774, a combination of three was selected for use in a portable miniature collection system. These three sorbent materials have complimentary adsorption characteristics as indicated by Table 9 and their δ_m ranges of utility. Therefore, this combination of sorbent materials was selected for incorporation into a multi-residue sampling system for collection of the twenty selected compounds. These three sorbents are listed below along with the major reasons for their selection.

Tenax-GC - The only high temperature (350°C) adsorbent available which allows the quantitative thermal desorption of low-volatility organic compounds.

Porapak R - One of the highest capacity polymeric adsorbents with a reasonable background level (better than Porapak N) and with an overlap in range of utility (δ_m) with Tenax-GC.

Ambersorb XE-340 - Less difficulty anticipated with the desorption of compounds of intermediate volatility, fewer detrimental effects by water and reactivity with collected samples than with charcoal. Also, its range of utility (δ_m) leaves the smallest gap between polymeric and carbonaceous adsorbents in the types of compounds collected.

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[47] Brooks, J. J., D. S. West, D. J. David, and J. D. Mulik. A Combination Sorbent System for Broad Range Organic Sampling in Air. In: Proceedings of the Symposium on the Development and Usage of Personal Monitors for Exposure and Health Effect Studies. EPA-600/9-79-032, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1979. 525 pp.

TABLE 11. ADSORBENT PROPERTIES CHART

Absorbent	Temp limit, °C	Cond[a] temp, °C	Des[b] temp, °C	Chemical composition	Major thermal decomposition products	Background level	Δp,[c] psig[d]	Capacity	Desorption	Range of utility, in terms of δ_m
Tenax-GC (35/60 mesh)	350	320	300	2,6-Diphenyl-p-phenylene oxide	Alkyl benzene Styrene Benzene Alkyl phenols	GOOD (none detected above system background)	~1.6	Should efficiently (trap intermediately (and less) volatile compounds with slightly less affinity for polar compounds.	Very amenable to thermal desorption for intermediately (and all higher) volatile compounds.	~950->2,800
Porapak R (50/80 mesh)	250	235	150 to 220	N-Vinyl pyrrolidone	Vinyl Pyrrolidone Pyrrolidone Pyrrilidiene	Air conditioning at 235°C, backupon desorbing is: POOR @ 220°C (well above system background) FAIR @ 150°C (slightly above system background)	~1.1[e]	Should efficiently trap intermediately (and less) volatile compounds with slightly greater affinity for polar	Very amenable to thermal desorption for intermediately (and all higher) volatile compounds.	~750-~1,500
Porapak N (50/80 mesh)	190	175	150	N-Vinyl pyrrolidone	Vinyl pyrrolidone Pyrrolidone Pyrrilidiene	POOR (Well above system background)	1.1	Should efficiently trap intermediately (and less) volatile compounds with slightly greater affinity for polar compounds.	Very amenable to thermal desorption for intermediately (and all higher) volatile compounds.	~750-~1,500
Ambersorb XE-340	>400	320	300	Carbonized styrene-divinyl benzene	None observed (after conditioning at 350°C + observed on GC/MS)	GOOD (None detected tected above system background)	0.6	Should efficiently trap highly (and all less) volatile compounds with greater affinity for polar compounds.	Questionable amenability to thermal desorption for all but highly volatile hydrocarbons.	~450-~750
SKC Activated charcoal	>400	320	300	Carbonized organics	None observed	GOOD (None detected above system background)	~0.6[e]	Should efficiently trap highly (and all less) volatile compounds with much greater affinity for polar compounds.	Questionable amenability to thermal desorption for all but highly volatile hydrocarbons.	~350-~600

[a] Conditioning.

[b] Desorption.

[c] Pressure drop across tapered tubes containing 1.0 g of adsorbent at a 3-liter/min flow rate.

[d] 1 psig = 6.9 x 10^3 Pa.

[e] Estimated.

SECTION 7

DEVELOPMENT OF THE ANALYTICAL METHOD

OBJECTIVE

The analytical technique determined to be most suitable for the determination of the twenty selected compounds was capillary gas chromatography ±(GC)^{2}1 combined with mass spectroscopy (MS). In order to be cost and time effective, it was decided that the capillary gas chromatographic technique should be developed prior to interfacing with a mass spectrometer. Ideally, this (GC)^{2} technique was to allow the separation of the twenty compounds of interest, to be adaptable to mass spectrometric detection, and to permit the introduction of sorbent tube samples obtained by either solvent or thermal desorption. This analytical technique was to be used for the laboratory development and evaluation of the multi-residue sampling system, as well as for the analyses of field samples (after MS interfacing).

INSTRUMENTATION

A Hewlett-Packard Model 5840 gas chromatograph (GC) was dedicated to this contract during the development of the analytical method. This instrument had dual flame ionization detectors (FID) and a printer/plotter terminal with microprocessing and integration capabilities. In addition, the instrument could be used with capillary GC columns, in either a split or splitless injection mode, and with packed GC columns. A liquid nitrogen cryogenic option was installed in the instrument during the course of the analytical method development work. This instrument was selected as being particularly suitable to this contract because a Hewlett-Packard Model 5985 GC/MS instrument was to be used for later analyses. The chromatograph on the GC/MS instrument is also a Hewlett-Packard Model 5840 GC, almost identical to the instrument selected for developing the analytical method.

EVALUATION

Columns

A variety of GC capillary columns were evaluated for their suitability for the analysis of the twenty selected compounds. Five columns were evaluated during the analytical method development work performed on the Hewlett-Packard Model 5840 GC; a few other columns were tried later during GC/MS interfacing and investigation of multi-detector GC analyses. The five columns investigated with the Hewlett-Packard Model 5840 GC included:

- An ∿48 m long, ∿0.25 mm ID, Carbowax 20 M wall-coated, open-tubular (WCOT) glass column.
- An ∿50 m long, ∿0.50 mm ID, Carbowax 20 M wall-coated, open-tubular, glass column.
- An ∿50 m long, ∿0.20 mm ID, Carbowax 20 M wall-coated, open-tubular, fused-silica column.
- An ∿50 m long, ∿0.20 mm ID, OV-101 wall-coated, open-tubular, fused-silica column.
- An ∿45 m long, ∿0.50 mm ID, SP2100 support-coated, open-tubular (SCOT), glass column.

These columns were coated with three types of liquid phases, Carbowax 20 M, OV-101, and SP2100. Carbowax 20 M is a polar phase, and OV-101 and SP2100 are non-polar methyl-silicone phases that are approximately equivalent. Different types of capillary columns also are represented by these five columns including a wide-bore SCOT glass column, a wide-bore WCOT glass column, a regular-bore WCOT glass column and two narrow-bore fused silica columns.

These columns were assessed for their ability to chromatograph the twenty compounds of interest by installing them within the GC using direct injection port and detector connections. The headspace samples or standard analytical mixtures of these compounds were injected into the GC. The results of these experiments are compiled in Table 12. Although chromatographic conditions were varied with the evaluation of each column, Table 12 still demonstrates the comparative abilities of the columns to chromatograph and separate the compounds of interest.

The retention times indicate the columns' abilities to separate these compounds. Compounds with retention time differences of less than ∿0.15 min usually co-eluted during the analysis of a mixture. For example, tetrachloroethylene (RT = 5.25 min) and acrylonitrile (RT = 5.27 min) were found to co-elute when analyzed together on an ∿0.25 mm ID, Carbowax 20 M WCOT column (column A in Table 12). All columns were found to have at least two co-eluting compounds, although which compounds co-eluted varied from column to column. To help separate compounds as best as they could be separated, all columns but one were evaluated using close to optimal conditions. These conditions included very slow temperature programming (2 or 3°C/min) from a low temperature (0° or 35°C) to an upper temperature ∿30°C below the columns' temperature limits. The exception was the wide-bore

TABLE 12. CHROMATOGRAPHIC PROPERTIES OF THE TWENTY SELECTED COMPOUNDS ON VARIOUS CAPILLARY COLUMNS

Compound	Column A		Column B		Column C		Column D		Column E	
	R.T., min	Peak shape	R.T., min	Peak shape	R.T., min	Peak shape	R.T., min	Peak shape	R.T., min	Peak shape
Propane[a]	2.84	1	NE	NE	NE	NE	NE	NE	3.09	1
Ethylene oxide	NE	NE	NE	NE	NE	NE	NE	NE	6.79	5
Acrolein	3.46	3	NE	NE	3.71	2	NE	NE	4.17	5
Carbon tetrachloride	3.63	2	NE	NE	3.88	1	NE	NE	8.22	3
Vinyl acetate	3.76	2	NE	NE	4.00	2	6.33	2	5.75	4
Benzene	4.06	1	NE	NE	4.39	2	9.10	1	8.11	2
Tetrachloroethylene	5.25	1	NE	NE	5.54	1	18.94	2	19.38	3
Acrylonitrile	5.27	3	NE	NE	5.12	2	5.54	2	8.38	5
Ethylene dichloride	5.99	2	NE	NE	6.72	1	8.51	2	7.35	3
1,4-Dioxane	6.25	2	NE	NE	6.41	2	11.51	2	4.22	2
Ethylene dibromide	14.77	2	NE	NE	NE	NE	17.97	2	17.71	3
cis-1,3-Dichloropropene	15.24	2	NE	NE	NE	NE	15.70	2	∿13	3
trans-1,3-Dichloropropene	9.26	2	NE	NE	NE	NE	13.70	2	NE	NE
Styrene	17.23	3	NE	NE	UN	2	25.82	2	23.74	3
Benzyl chloride	34.76	3	NE	NE	UN	2	36.48	2	27.87	2
Ethylene glycol[b]	39.44	4	2.78	2	UN	3	86.45	2	20.10	5
Hexachloro-1,3-butadiene	40.22	2	3.72	2	UN	2	53.49	2	31.79	3
Toluene-2,4-diamine	84.83	3	2.69	2	NE	NE	68.67	2	34.71	5
Di-(2-ethylhexyl)phthalate	133.01	2	NE	NE	UN	2	151.73	3	∿26	5
Pentachlorophenol	ND	ND	>95	3	ND	ND	ND	ND	38.56	3
Benzidine	ND	ND	ND	ND	ND	ND	111.21	2	48.33	5
Chrysene	ND	ND	NE	NE	ND	ND	131.15	3	64.66	3
Benzo(a)pyrene	ND	ND	NE	NE	ND	ND	213.03	4	∿107	4

[a] Propane was used to determine column dead volume.

[b] Ethylene glycol is a polymerization product of ethylene oxide.

KEY

NE - Not evaluated
ND - Not detected
UN - Unknown
RT - Retention time

Peak Shape:

1 - Excellent
2 - Good
3 - Fair
4 - Poor
5 - Very poor

Columns:

A - Carbowax 20 M wall-coated, open-tubular, glass column, ∿0.25 mm ID, ∿48 m long
B - Carbowax 20 M wall-coated, open-tubular, glass column, ∿0.50 mm ID, ∿50 m long
C - Carbowax 20 M wall-coated, open-tubular, fused-silica column, ∿0.20 mm ID, ∿50 m long
D - OV-101 wall-coated, open-tubular, fused-silica column, ∿0.2 mm ID, ∿50 m long
E - SP2100 support-coated, open-tubular, glass column, 0.50 mm ID, ∿45 m long

(~0.50 mm ID) Carbowax 20 M WCOT column (column B in Table 12). Column B was evaluated isothermally near its upper temperature limit to determine whether high-boiling compounds such as di-(2-ethylhexyl) phthalate and pentachlorophenol would elute significantly faster (in less than ~60 min) than from a similar narrow-bore column (column A). Unfortunately, these high-boiling compounds did not quickly elute from the wide-bore column (column B) either. Indeed, all compounds in Table 12 indicated as "not detected" did not appear to elute during the analysis time allotted (100 to 220 min). High boiling compounds did not appear to elute from any of the Carbowax 20 M coated capillary columns under the analytical conditions evaluated.

How a column interacts with a compound eluting through it is demonstrated by the peak shape of the resulting chromatogram. A very sharp, well-shaped peak indicates "good" chromatographic interaction, whereas a tailing, broad, or skewed peak indicates "poor" chromatographic interaction. The chromatographic interactions of the twenty selected compounds with the various capillary columns were evaluated by rating the peak shapes of their chromatograms as indicated in Table 12. Generally, tailing was the major problem observed and ranged from slight to very extreme. A peak shape rating of at least a 3 (Fair), preferably a 2 (Good), was considered adequate for permitting compound quantitation. The SCOT column (Column E) demonstrated the poorest chromatographic ability with badly tailing peaks observed for polar compounds such as ethylene oxide, acrylonitrile, and ethylene glycol. All of the other columns exhibited reasonable chromatograms for most of the compounds with the fused-silica column giving especially good results.

As a result of these analyses, ethylene oxide was eliminated from the list of compounds to be investigated because it so readily reacted to form ethylene glycol and other products. Instead, both of the isomers of 1,3-dichloropropene were to be evaluated. Ethylene glycol was included in most of the subsequent analyses as a compound which might be of interest later. Although ethylene glycol doesn't exhibit carcinogenic potential [1], its presence in a sample could indicate the possible presence of ethylene oxide.

Column test mixtures, as suggested in the literature [48], were prepared to further evaluate the performance of the capillary columns. These mixtures are given in Tables 13 and 14 and typical chromatograms are shown in Figures 3 and 4. They were useful in evaluating a number of chromatographic phenomena arising from column and system characteristics. Specifically, the normal

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[48] Cram, S. P., F. J. Yang, A. C. Brown III. Characterization of High Performance Glass Capillary Gas Chromatography. Chromatographia, 10(8), 1977.

TABLE 13. COMPOSITION OF COLUMN TEXT MIXTURE IIb

Compound	M.W., g/mol	Density, g/mL	Amount in 10 mL MeOH, mg	Conc., ppm (wt/wt)	Amount in 1 mL inj., µg	Amount to (GC)^2 Det.,[a] ng
C_{12}	170.33	0.751	28.9	3,910	3.10	15.5
C_{13}	184.36	0.757	13.3	3,645	2.89	14.5
DMA	121.18	0.974	18.7	2,359	1.87	9.4
DMP	122.16	1.036	15.7	1,980	1.57	7.9
2-Ethyl hexanol	130.23	0.834	31.6	3,986	3.16	15.8
Naphthalene	128.16	1.145	31.0	3,910	3.10	15.5
2-Octanone	128.21	0.818	18.0	2,270	1.80	9.00
MeOH[b]	32.04	0.793	-	-	-	-

[a] Assuming a 200 to 1 split ratio.

[b] Solvent.

TABLE 14. COMPOSITION OF COLUMN TEST MIXTURE IIIa

Compound	Concentration, µg/mL	Amount in 1 µL injection, ng	Amount to detector,[a] ng
n-C_{10}	312	312	3.12
n-C_{13}	346	346	3.46
n-C_{16}	356	356	3.56
n-C_{18}	158	158	1.58
n-C_{20}	304	304	3.04
Dimethylphenol (DMP)	200	200	2.00
Dimethylaniline (DMA)	570	570	5.70
2-Octanone	314	314	3.14
2-Ethyl hexanol	300	300	3.00
Acetone[b]			

[a] Assuming a 100:1 split ratio.

[b] Solvent.

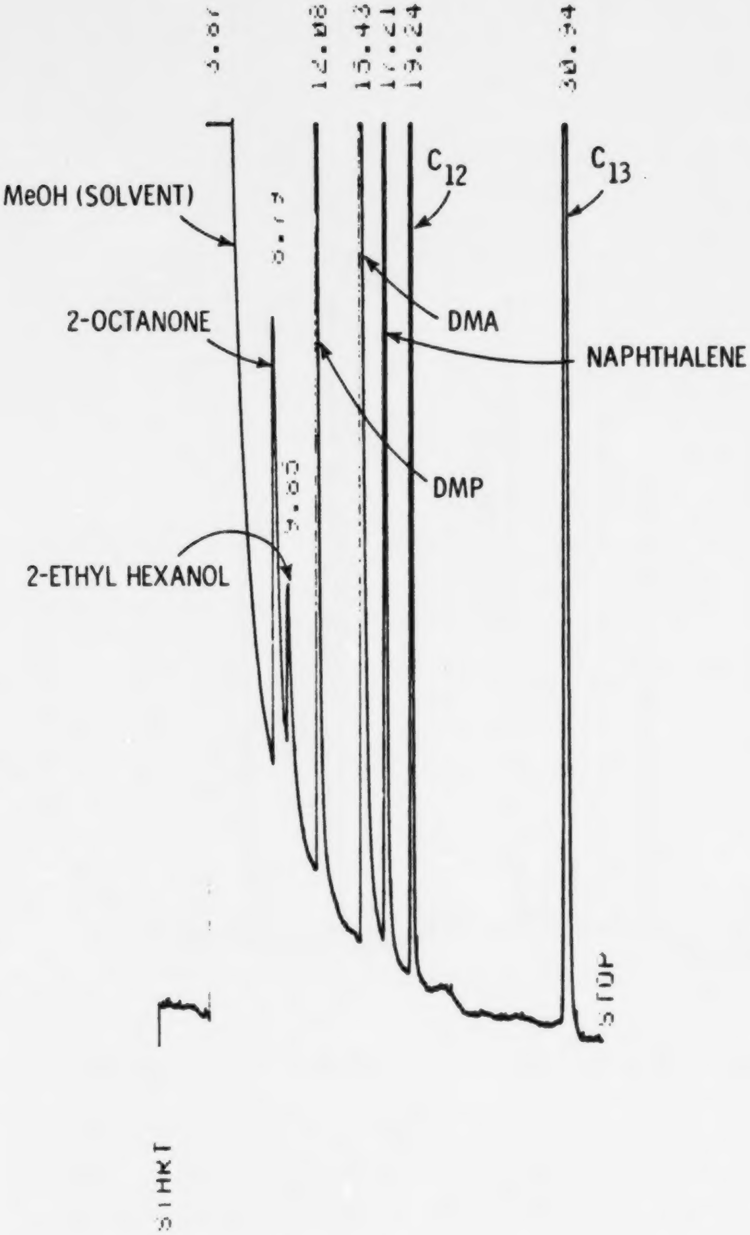


Figure 3. Chromatogram of column test mixture IIb.

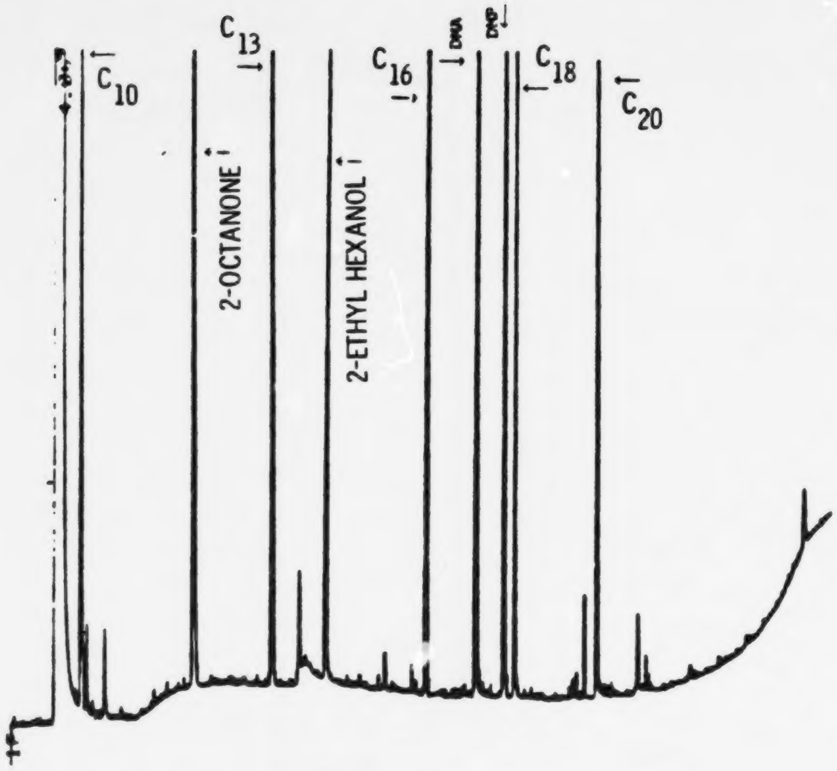


Figure 4. Chromatograms of column test mixture IIIa.

alkanes were used to characterize instrumental band-broadening effects and to calculate column parameters such as theoretical plates and separation number. Adsorption effects were indicated by naphthalene, 2-octanone, and 2-ethyl hexanol. Naphthalene tails in the presence of any metal adsorptive sites, 2-octonone tails in the presence of surfaces or interfaces which act as Lewis acids, and the alcohol (2-ethyl hexanol) indicates active siloxyl groups on glass capillary surfaces. The acid-base pair, 2,6-dimethylaniline (DMA) and 2,6-dimethylphenol (DMP), were used to determine the acidity/basicity of the capillary columns.

The chromatographic performances of the various capillary columns determined by these columns test mixtures is compiled in Table 15. Generally, all of the columns demonstrated little or no tailing for the alcohol and ketone peaks unless the column was deteriorated due to age. Naphthalene was removed from the second test mixture because the capillary inlet system (to be discussed shortly) showed no major problems with adsorptive metal sites and because directly connecting the capillary columns to the GC injection port and detection eliminated metal unions. Chromatographic efficiency (as demonstrated by HETP in Table 15) was particularly good on the Carbowax 20 M WCOT column (column A) and the OV-101 fused-silica column (column D).

The ease of installing the chromatographic columns was also an important consideration. During the evaluation of the five columns all were directly connected to the GC detector and injection port. This is the "preferred" method of installing capillary columns because it eliminates active sites and dead volumes in various types of unions, such as unions made with heat-shrink Teflon tubing or low-dead volume stainless steel fittings. To install a glass column in a GC in this manner, the ends of the glass capillaries needed to be carefully straightened, cleaned, and deactivated. During the installation of the glass columns, extreme care had to be taken not to break their ends, or the procedure of straightening had to be repeated. The wide-bore glass columns were especially brittle. By comparison, the installation of the fused-silica columns was extremely simple and rapid. The outer polymeric coating and thin walls of the fused-silica columns gave them great enough flexibility and strength to be directly connected to the GC without prior preparations and without much risk of breakage.

Chromatographic Conditions

Flow rates through a capillary column are very small, ranging from ∿0.7 mL/min to ∿5 mL/min depending on the internal diameter of the column, the type of carrier gas, and column temperature. To get maximum chromatographic efficiency from any particular column an optimum range of flow rate exists which is described by a

TABLE 15. CHROMATOGRAPHIC PERFORMANCE OF VARIOUS CAPILLARY COLUMNS

Column	Compound	Theoretical plates, N, plates	HETP, mm/plate	Separation number		DMA/DMP ratio
				Compounds	No. of peaks	
A	n-Tridecane	∿160,000	∿0.3	NE	NE	1.18/1
B	n-Eicosane	∿37,000	∿1.1	NE	NE	NE
C	n-Eicosane	∿68,000	∿0.7	n-Octadecane &n-Eicosane	48	1.31/1
D	n-Eicosane	∿160,000	∿0.3	n-Octadecane &n-Eicosane	39	NE
E	n-Tridecane	∿74,000	∿0.6	n-Dodecane &n-Tridecane	26	0.84/1

Calculations:

$$\text{N, plates} = [(\text{RT, min})/(\text{W1/2H, min})]^2\ 5.54$$
$$\text{HETP, mm/plate} = (\text{L, mm})/(\text{N, plates})$$

KEY TO TABLE AND EQUATIONS:

NE - Not evaluated.
HETP - Height equivalent of a theoretical plate
DMA - 2,6-Dimethylaniline
DMP - 2,6-Dimethylphenol
N - Theoretical plates
L - Column length
RT - Retention time of compound
W1/2H - Width at half height of compound

Columns:

A - Carbowax 20 M wall-coated, open-tubular, glass column, ∿0.25 mm ID, ∿48 m long
B - Carbowax 20 M wall-coated, open-tubular glass column, ∿0.50 mm ID, ∿50 m long
C - Carbowax 20 M wall-coated, open-tubular, fused-silica column, ∿0.20 mm ID, ∿50 m long
D - OV-101 wall-coated, open-tubular, fused-silica column, ∿0.20 mm ID, ∿50 m long
E - SP2100 support-coated, open-tubular, glass column, ∿0.50 mm ID, ∿45 m long

Van Deemter plot. Such a plot, shown in Figure 5, was determined for the SP2100 SCOT column. Injections of propane were used to determine dead time at various column flow rates. By dividing the column length by the retention times of propane, the linear velocities were calculated. Analyses of column test mixture IIa were performed at each of these linear velocities. The height equivalents of a theoretical plate (HETP) were calculated for n-tridecane and plotted versus the linear velocities. An optimum in chromatographic efficiency occurs at a linear velocity of ∿20 cm/sec. The relationship of linear velocity, column flow rate, split flow rate, split ratio, and GC oven temperature was investigated. These values were determined at a number of GC oven temperatures and plotted in Figure 6. This demonstrates that for a temperature programmed analysis, the linear velocity decreases as oven temperature increases, affecting the column resolution during the course of the analysis. A linear velocity of ∿17 cm/sec at the upper GC temperature usually provided optimal flow rate conditions during the course of a temperature-programmed analysis. This usually corresponded to a flow rate of ∿0.8 to ∿1.2 mL/min at this upper temperature. At the lower temperature (0°C to 35°C) flow rates ranged from ∿1.2 to ∿2.0 mL/min for narrow and regular bore columns, and ∿3 to ∿6 mL/min for wide-bore columns. (Capillary column flow rate is controlled by column head pressure on an HP Model 5840 GC, which results in changing flow rates during temperature programming. Other instruments, however, have flow controllers which can maintain a constant, optimal flow rate throughout a temperature-programmed analysis.)

Isothermal analyses of a mixture of low boiling compounds [Standard Mixture $(GC)^2$Va] were performed at various temperatures to determine whether maintaining sub-ambient temperatures could improve chromatographic resolution. A typical chromatogram of this mixture is depicted in Figure 7. Two isothermal analyses of this mixture, at 40°C and at 5°C, are shown in Figure 8. As indicated by the resolution of 1,4-dioxane and ethylene dichloride, the analysis at 40°C provides better compound separation. The reduced chromatographic efficiency at the lower temperature was thought to be due to a combination of faster linear velocity and decreased effectiveness of the column liquid phase (in this case Carbowax 20 M), which has a lower temperature limit of 60°C. Therefore, maintaining a sub-ambient temperature for a long time (>10 min) was found not to improve chromatographic resolution. Slow temperature programming (2 to 3°C/min) from sub-ambient to higher temperatures generally produced the best chromatographic results.

Capillary Inlet System

The analytical method developed for this contract was to allow the introduction of sorbent tube samples obtained by either solvent or thermal desorption. Of course, a solvent desorbed sample

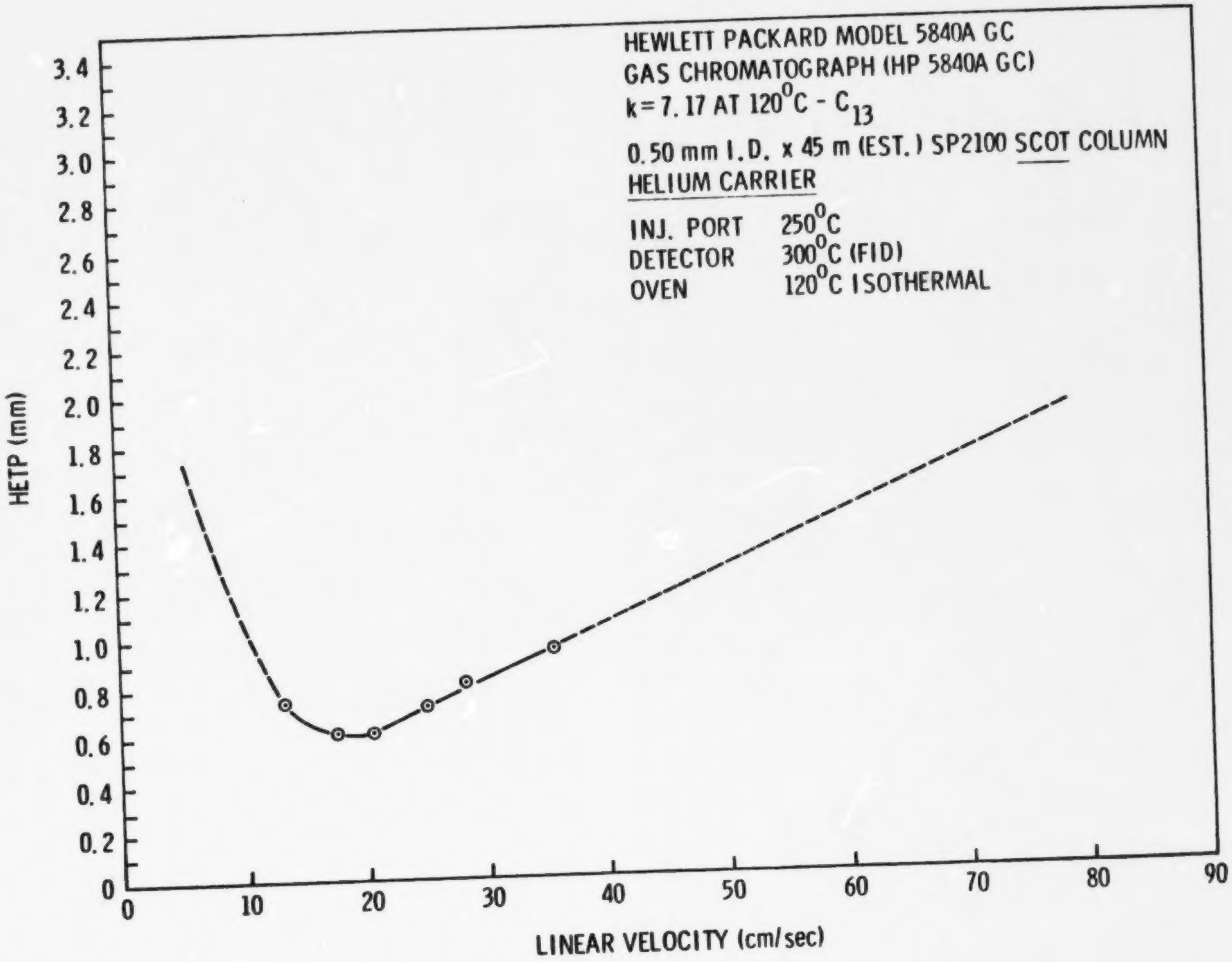


Figure 5. Van Deemter plot for analytical column.

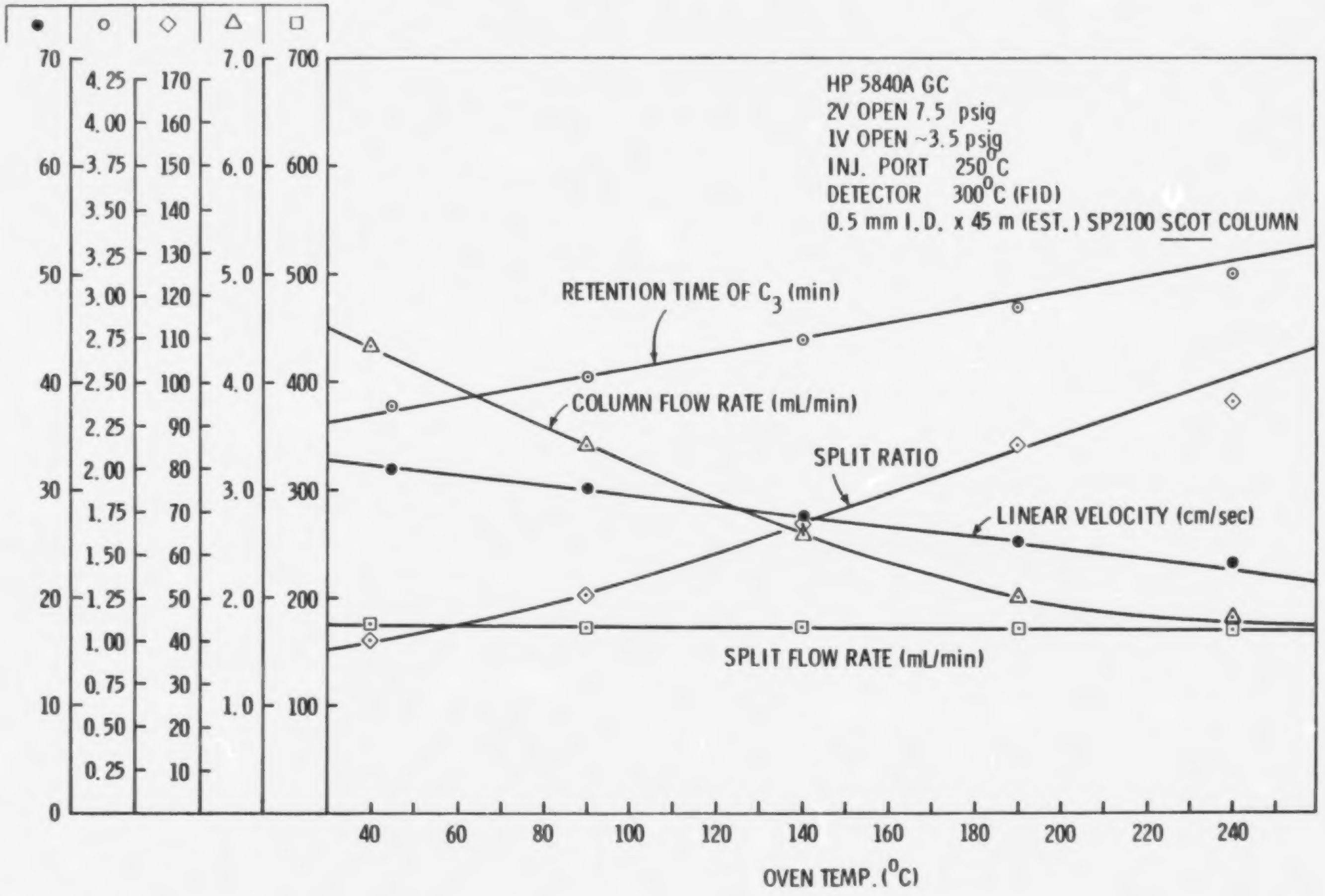


Figure 6. Effect of oven temperature on flow rates and linear velocity.

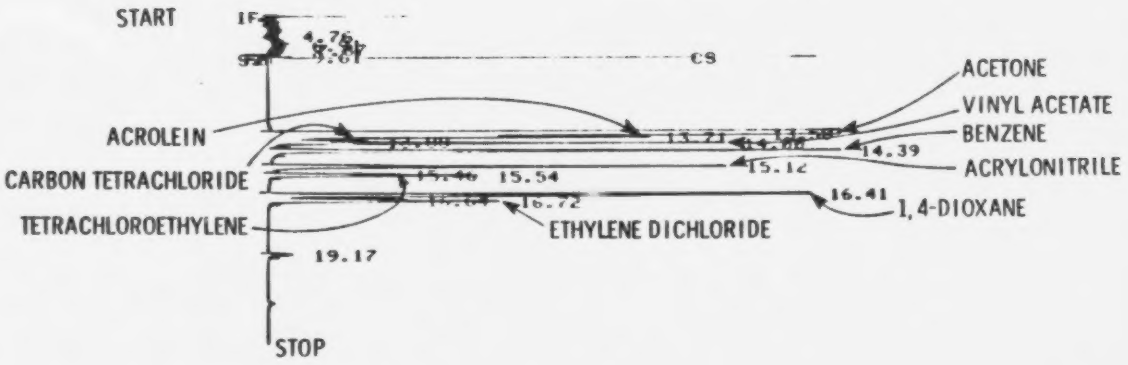
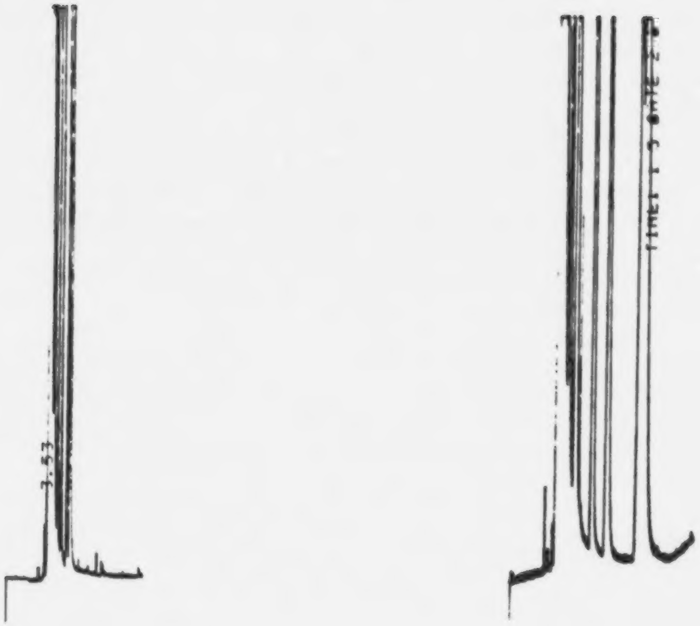


Figure 7. Typical chromatogram of Standard Mixture (GC)²Va.



A. 40°C isothermal analysis

B. 5°C isothermal analysis

Figure 8. Chromatograms of Standard Mixture $(GC)^2Va$.

can be introduced into a chromatograph by syringe injection. However, a thermally desorbed sorbent sample must be reconcentrated as it is slowly desorbing from a sorbent tube so that the entire sample can be introduced into the GC as a discrete slug. Such a discrete slug retains the chromatographic resolution capabilities of the analytical system.

An inlet system was designed and constructed to permit the thermal desorption of sorbent tubes, reconcentration of the desorbed of the desorbed samples in a trap, and the introduction of these samples into the capillary GC for analysis. The system was comprised of three major parts: a six-port, two-position high temperature valve; a sorbent-tube desorption chamber; and, a nickel capillary trap. A schematic of this system is shown in Figure 9. In the "trap" position a sorbent tube was desorbed by the tube furnace and its sample swept by the auxiliary "desorption" carrier through the valve into the nickel capillary trap, which was ~50% submerged in liquid nitrogen. The flow out of the trap was passed through the "A" injection port to the "A" FID for monitoring trap break-through. When the valve was switched to the "analyze" position, simultaneously the tube furnace was cooled, the liquid nitrogen was removed from the trap, and the trap was heated. The auxiliary "purge trap" flow then swept the collected sample out of the trap and into the capillary injection port. When the capillary GC was operated in the "split" mode, most of the sample entering the injection port was vented and only a small portion entered the capillary column for chromatographic separation and analysis. In this injection mode, vented portions of samples could be recollected onto other sorbent tubes for subsequent analyses.

The auxiliary "desorption" carrier was obtained simply by splitting flow off the instrument carrier supply line. However, the auxiliary "purge trap" carrier, which was responsible for sweeping a sample from the nickel capillary trap into the capillary injection port, was controlled by the capillary injection port pneumatics. This was accomplished, as sketched in Figure 10, by installing a tee after toggle valve 1. In this configuration part of the injection port carrier would purge the capillary inlet trap and introduce samples into the injection port through a needle. The rest of the injection port carrier would purge the GC injection port in a normal manner, sweeping the introduced (through the needle) sample into the GC capillary column.

Initially, thermal desportion of sorbent tubes was accomplished by a copper tube furnace wrapped with nichrome heating wire. A thermocouple was incorporated with this furnace and the unit was wrapped with asbestos and/or glass tape insulation. The temperature of this tube furnace was controlled by a Variac, and was capable of ballistic heating and cooling. A digital voltmeter was used to measure the furnace's temperature. Although the ballistic heating and cooling capabilities of this type of furnace were found to be excellent, after constant use and manipulation,

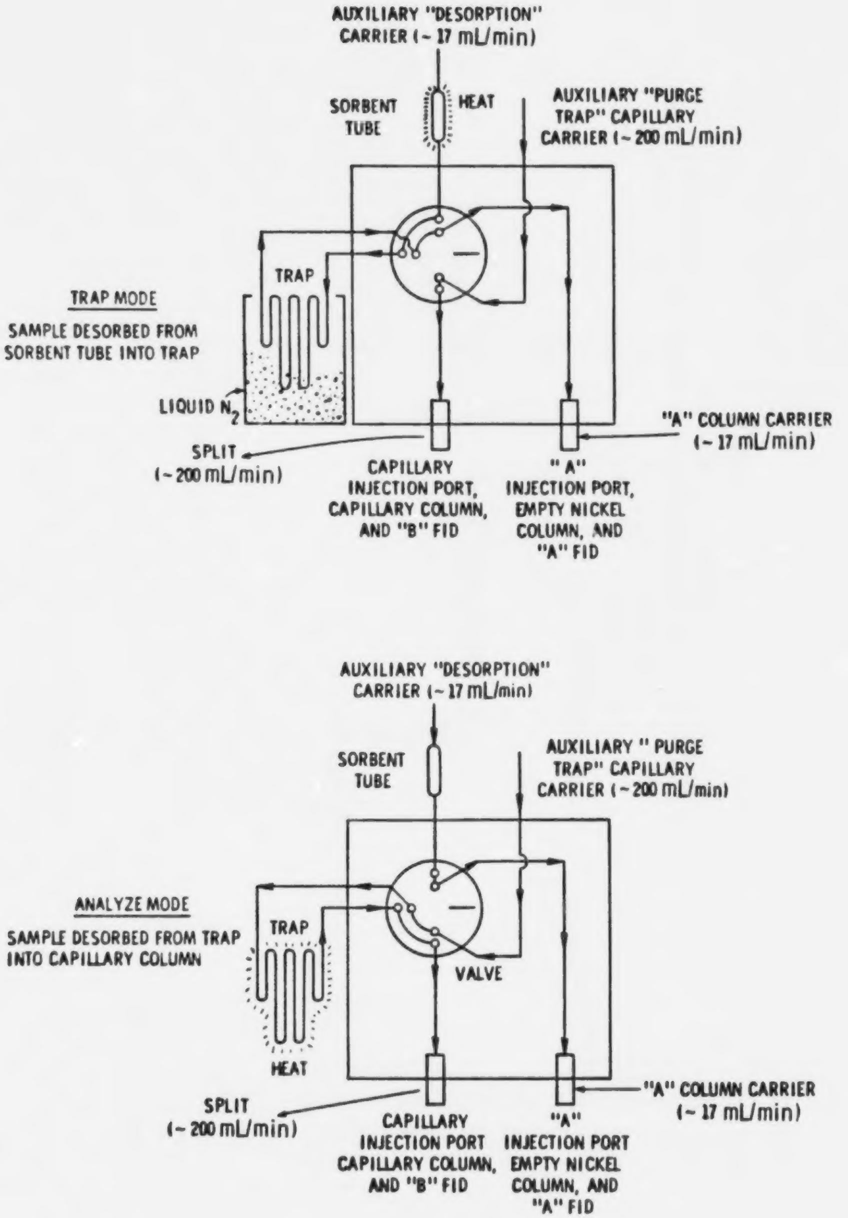

AUXILIARY "DESORPTION" CARRIER (~ 17 mL/min)
SORBENT TUBE
HEAT
AUXILIARY "PURGE TRAP" CAPILLARY CARRIER (~ 200 mL/min)
TRAP
TRAP MODE
SAMPLE DESORBED FROM SORBENT TUBE INTO TRAP
LIQUID N2
"A" COLUMN CARRIER (~ 17 mL/min)
SPLIT (~ 200 mL/min)
CAPILLARY INJECTION PORT, CAPILLARY COLUMN, AND "B" FID
"A" INJECTION PORT, EMPTY NICKEL COLUMN, AND "A" FID
AUXILIARY "DESORPTION" CARRIER (~ 17 mL/min)
SORBENT TUBE
AUXILIARY " PURGE TRAP" CAPILLARY CARRIER (~ 200 mL/min)
ANALYZE MODE
SAMPLE DESORBED FROM TRAP INTO CAPILLARY COLUMN
TRAP
VALVE
HEAT
"A" COLUMN CARRIER (~ 17 mL/min)
SPLIT (~ 200 mL/min)
CAPILLARY INJECTION PORT CAPILLARY COLUMN, AND "B" FID
"A" INJECTION PORT EMPTY NICKEL COLUMN, AND "A" FID

Figure 9. Flow schematic of capillary inlet system.

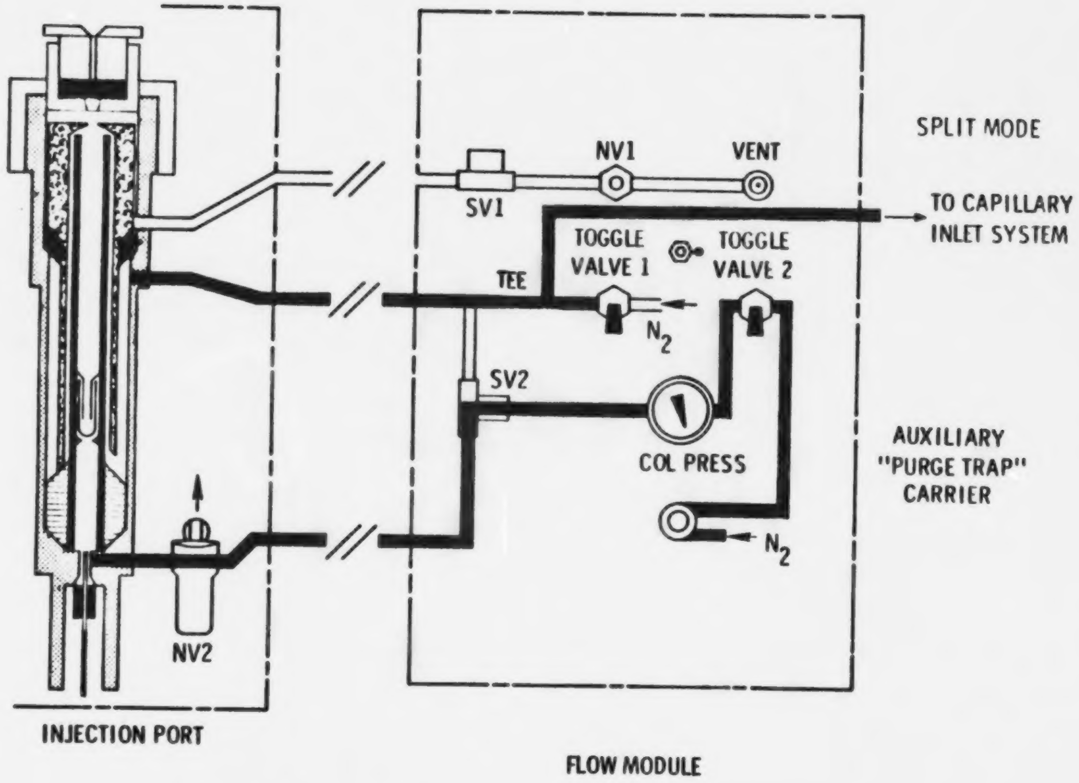

SPLIT MODE
NV1
VENT
SV1
TO CAPILLARY INLET SYSTEM
TOGGLE VALVE 1
TOGGLE VALVE 2
TEE
N_2
SV2
COL PRESS
AUXILIARY "PURGE TRAP" CARRIER
N_2
NV2
INJECTION PORT
FLOW MODULE

Figure 10. Schematic of flow pattern at the capillary GC injection port.

the insulation of the furnace would deteriorate and the thermocouple would short to the heating wire. Consequently a different, more durable, desorption chamber was designed and constructed. This desorption chamber is pictured in Figure 11. It consisted of an electrically heated aluminum block hinged in two halves with each half provided with its own thermocouple and heating element. Sorbent tubes were desorbed by being placed in the center of this device with its hinged "doors" enclosed around them. The advantages of this desorption chamber included:

- Easy mounting/dismounting of the entire unit by attachment/detachment of its mounting bars to a ring stand;
- Ballistic heating and cooling of sorbent tubes by closing and opening the chamber's hinged doors, while maintaining the aluminum block at desorption temperatures;
- Durability due to the sturdiness of design (fragile parts embedded in the aluminum block) and simplicity of frequent manipulation (just open "doors" to change sorbent tubes); and
- Non-interference with sample analyses since the chamber was not within the desorption flow system.

Another improvement made to the capillary inlet system was the design and construction of a thermal control unit, sketched in Figure 12. This unit could accommodate all of the heating requirements of the capillary inlet system, including power supply and thermocouple monitoring. Five voltage regulators were used to supply power to the various parts of the capillary inlet system, replacing the Variacs that were previously used to perform this function. A transformer used to heat the nickel capillary trap by electrical resistance was incorporated into the thermal control unit. The voltage regulators are controlled by on/off switches, of which two can be activated/deactivated by timing devices. Desorption of the nickel trap by resistive heating was usually controlled by one of these timers to prevent the transformer from overheating. Pilot lights were also included to indicate the status of the on/off switches and intensity indicator lamps visually displayed the voltage settings of the regulators. A pyrometer attached to a multi-position selector switch permitted the alternate monitoring of up to twelve thermocouples. A sketch of the "improved" capillary inlet system is given in Figure 13.

Another improvement to the capillary inlet system, made after and as a result of analytical method development experiments and evaluation of sorbent tubes, was a slight change in the design of the nickel capillary trap. The two trap designs are shown in Figure 14. Note that the major difference in the two designs is that the "newer" trap has zones both above and below

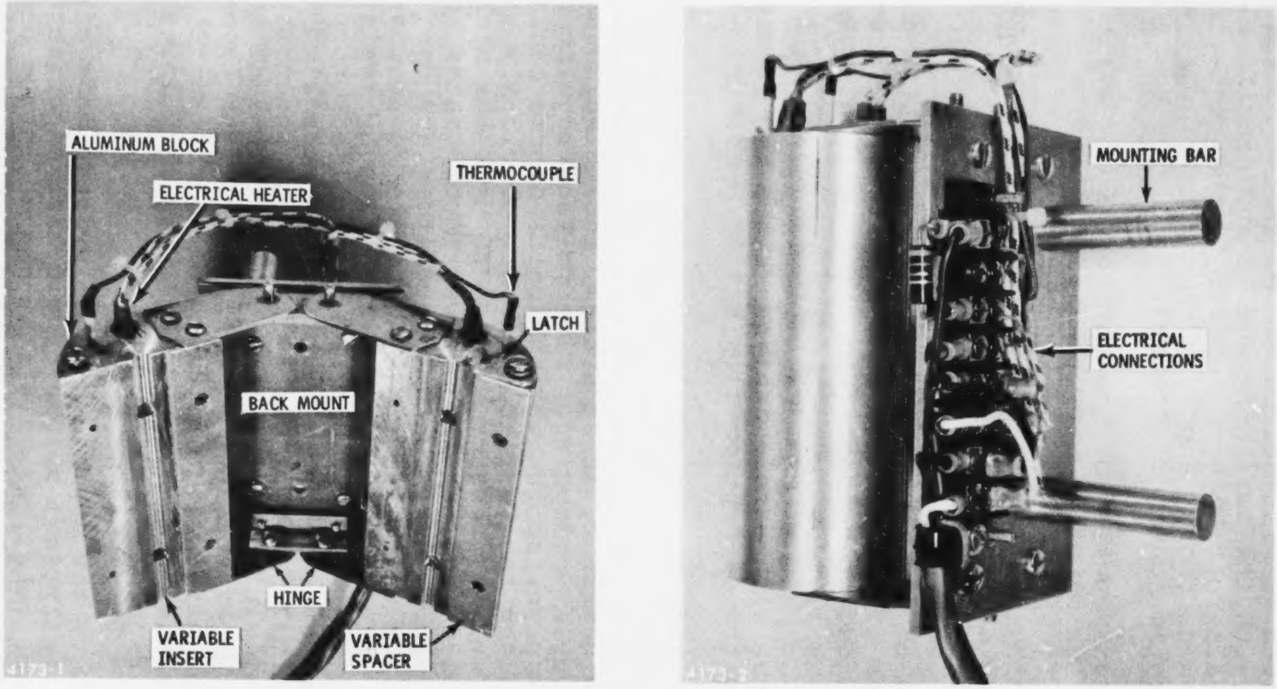

ALUMINUM BLOCK
ELECTRICAL HEATER
THERMOCOUPLE
LATCH
BACK MOUNT
HINGE
VARIABLE INSERT
VARIABLE SPACER
4173-1
MOUNTING BAR
ELECTRICAL CONNECTIONS
4173-2

Figure 11. Front and rear view photograph of new, durable capillary inlet system desorption chamber.

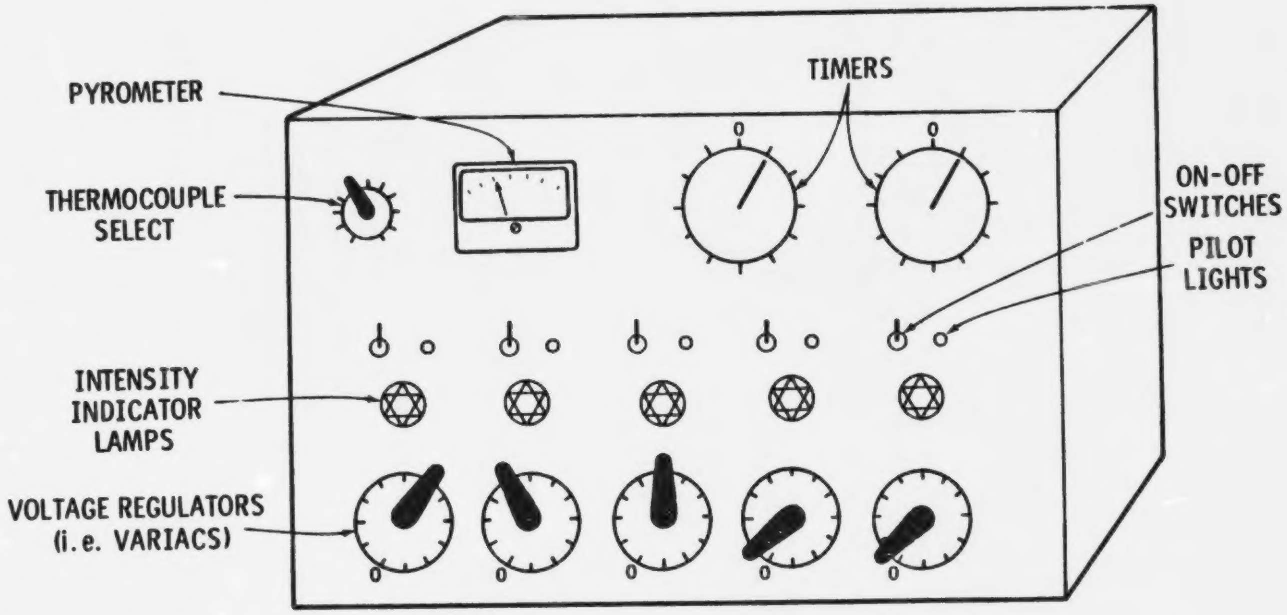
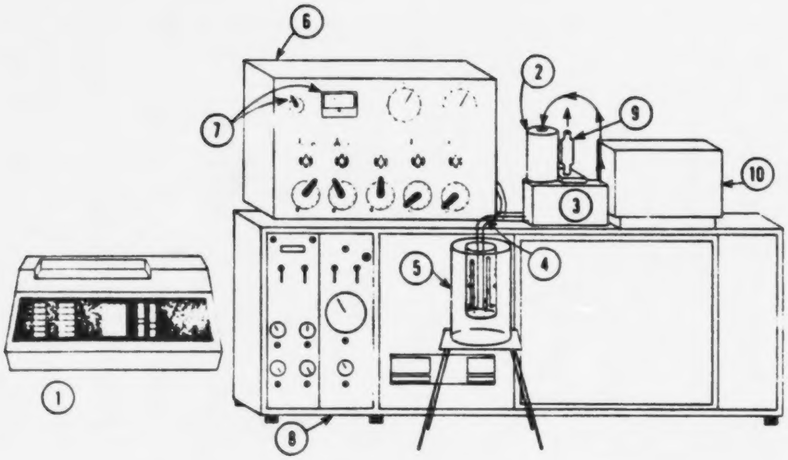

PYROMETER
TIMERS
THERMOCOUPLE SELECT
ON-OFF SWITCHES
PILOT LIGHTS
INTENSITY INDICATOR LAMPS
VOLTAGE REGULATORS (i.e. VARIACS)
0
0
0
0
0
0
0

Figure 12. Sketch of capillary inlet system thermal control unit.



① HEWLETT-PACKARD MODEL 5840A GC WITH GLASS CAPILLARY OPTION

② TUBE DESORPTION CHAMBER (OVEN)

③ HEATED VALVE OVEN-CONTAINING 6-PORT, 2-POSITION, LOW DEAD VOLUME VALVE

④ 1-METER, Ni CAPILLARY TRANSAXIAL TRAP

⑤ DEWAR CONTAINING LIQUID N_2 FOR COOLING CAPILLARY TRAP

⑥ THERMAL CONTROLLER FOR INSTANT HEATING OF CAPILLARY TRAP, HEATING DESORPTION CHAMBER HEATING VALVE, ETC.

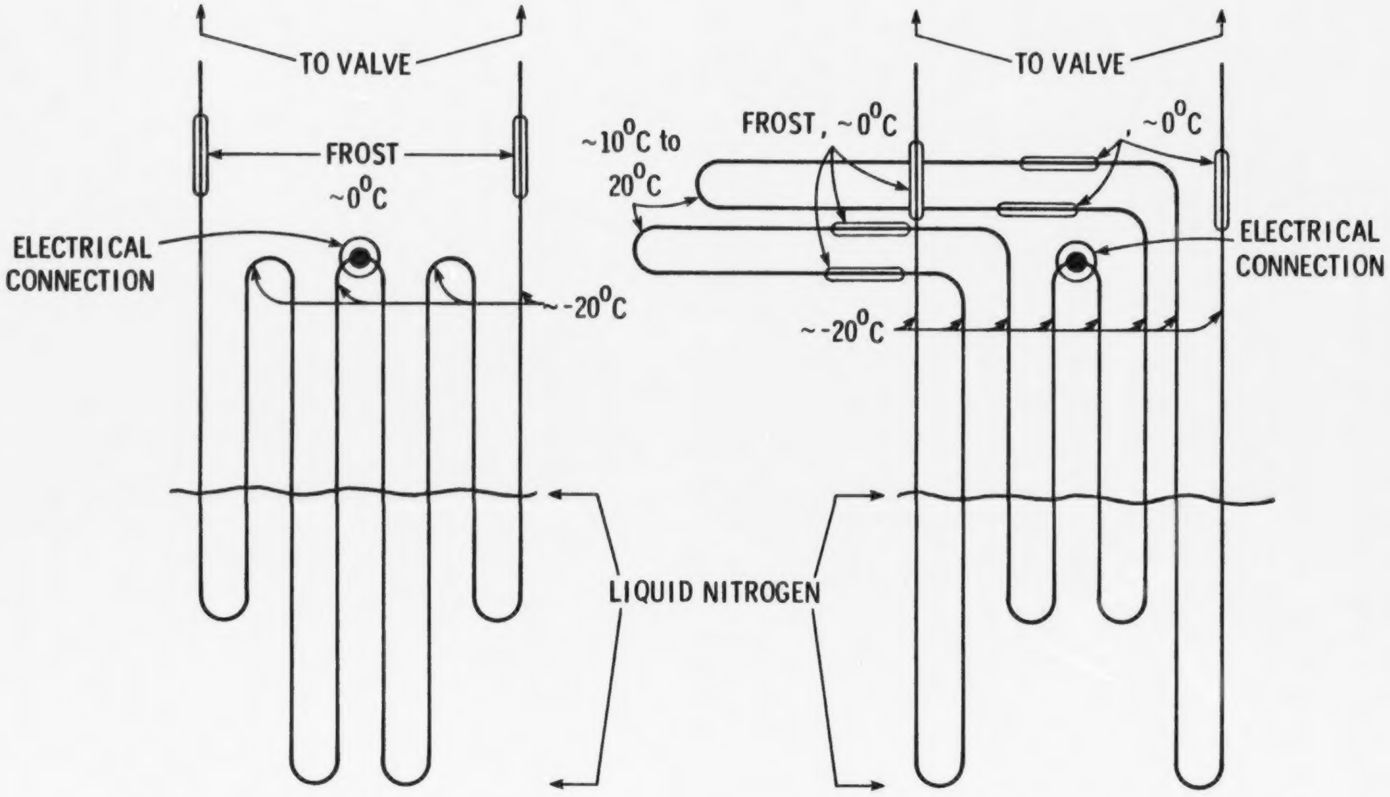
⑦ PYROMETER FOR TEMPERATURE READINGS WITH MULTI-POSITION SELECTOR

⑧ FLOW CONTROLLERS AND SPLIT CONTROLLER

⑨ RECOLLECTION VENT WITH TUBE

⑩ DETECTOR ADAPTABLE TO FID, N-P FID, GLASS JET FID

Figure 13. Capillary GC with capillary inlet system.


TO VALVE
FROST
~0°C
ELECTRICAL CONNECTION
~-20°C
LIQUID NITROGEN
~10°C to 20°C
FROST, ~0°C
, ~0°C
TO VALVE
ELECTRICAL CONNECTION
~-20°C

A. "OLD Ni CAPILLARY TRAP DESIGN
(~1 meter LONG x ~0.76 mm I.D.)

B. "NEW" Ni CAPILLARY TRAP DESIGN
(~1.5 meter LONG x ~0.51 mm I.D.)

Figure 14. Comparison of trap designs and their temperature zones during cryogenic sample reconcentration.

0°C during cryogenic sample reconcentration. This was found to reduce the problem of cryogenic trap breakthrough due to the presence of significant levels of water in samples.

The effect of this capillary inlet system on the chromatographic performance of the analytical system was evaluated by analyzing samples of the column test mixtures previously described. Immediately prior to installing the capillary inlet system on the GC, a test mixture would be analyzed to provide a basis for comparing results. Once the system was installed and demonstrated to be free of leaks, samples of the column test mixture were injected into the inlet system. These injections were either made into a stainless steel injection oven (installed in place of the sorbent tube desorption chamber) or through a tee into an empty glass tube enclosed by the desorption chamber (Figure 15). These samples were then cryogenically reconcentrated in the nickel trap before being introduced into the GC. The results of these evaluations are given in Table 16. The reproducibility of results for several injections of Standard Mixture Va (Figure 7) was also evaluated. Injections were made through a tee into a heated empty glass tube (Figure 15). Tables 17 and 18 summarize the results obtained. Overall, the capillary inlet system appeared to perform very well. Reproducibility for standards was reasonably good, the effect on chromatographic efficiency was slight, and no noticable difference in peak shapes were noted for any of the twenty selected compounds or the compounds in the column test mixtures.

Injection Mode

In order to detect between 1 and 100 parts per trillion concentrations of various compounds in ambient air, one must be able to collect at least 10 ng of a compound and then detect this amount (10 ng) or less during sample analysis. To obtain maximum sensitivity for an analysis, the entire sample contained on a sorbent tube should be introduced into the capillary column (after cryogenic reconcentration) by using the "splitless" injection mode. However, such a "one-shot" analysis does not permit a sorbent tube sample to be split and part recollected on another sorbent tube for additional analyses. Therefore, analytical sensitivity must be weighed against the requirement for multiple sample analyses for any application.

The flame ionization detectors of the Hewlett-Packard Model 5840 GC were estimated to have a detection limit of 0.01 ng to 1 ng for most compounds. Therefore most laboratory evaluations were conducted with the GC in the "split" injection mode, usually with a split ratio of 100 to 1. The "splitless" mode of sample introduction, however, was briefly investigated to evaluate the performance of the analytical system under these conditions. Two problems were noted. One was the analytical interference of the solvent with the compounds of interest in standard

TABLE 16. EFFECT OF CAPILLARY INLET SYSTEM ON THE CHROMATOGRAPHIC PERFORMANCE OF VARIOUS CAPILLARY COLUMNS

Inlet system	Trap design	Column	Compound	Theoretical plates, N, plates	HETP, mm/plate
No		A	n-Tridecane	~160,000	~0.3
Yes	"Old"	A	n-Tridecane	~84,000	~0.6
No		D	n-Octadecane	~150,000	~0.3
Yes	"New"	D	n-Octadecane	~53,000	~0.9
No		E	n-Tridecane	~74,000	~0.6
Yes	"Old"	E	n-Tridecane	~68,000	~0.7

Calculations:

N, plate = [(RT, min)/(W1/2H, min)]^2 5.54
HETP, mm/plate = (L, mm)/(N, plates)

KEY TO TABLE AND CALCULATIONS:

HETP - Height equivalent of a theoretical plate
N - Theoretical plates
RT - Retention time of compound
W1/2H - Width at half height of compound
L - Column length

Columns:

A - Carbowax 20 M wall-coated, open-tubular, glass column, ~0.25 mm ID, ~48 m long
D - OV-101 wall-coated, open tubular, fused-silica column, ~0.20 mm ID, ~50 m long
E - SP2100 support-coated, open-tubular, glass column, ~0.50 mm ID, ~45 m long

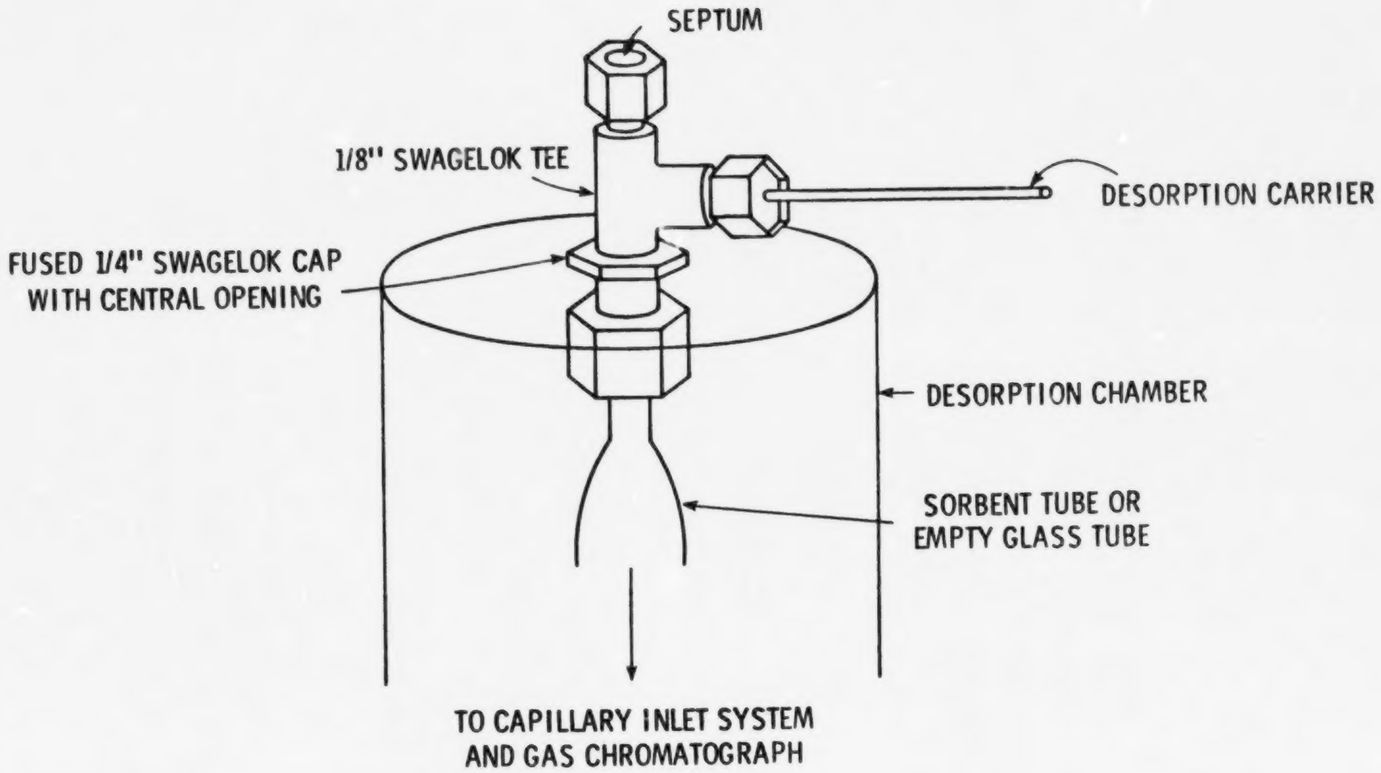

SEPTUM
1/8" SWAGELOK TEE
DESORPTION CARRIER
FUSED 1/4" SWAGELOK CAP
WITH CENTRAL OPENING
DESORPTION CHAMBER
SORBENT TUBE OR
EMPTY GLASS TUBE
TO CAPILLARY INLET SYSTEM
AND GAS CHROMATOGRAPH

Figure 15. Injection system with modified septum tee.

TABLE 17. REPRODUCIBILITY OF RETENTION TIMES

Compound	Retention times, min[a]						Statistics	
	Run #468	Run #469	Run #470	Run #471	Run #472	Run #473	Mean	RSD[b], %
Acetone (solvent)	3.60	3.60	3.60	3.59	3.58	3.58	3.59	0.3
Acrolein	3.74	3.74	3.75	3.73	3.72	3.71	3.73	0.4
Carbon tetrachloride	3.92	3.92	3.92	3.90	3.89	3.88	3.91	0.5
Vinyl acetate	4.05	4.05	4.05	4.03	4.01	4.00	4.03	0.6
Benzene	4.46	4.46	4.45	4.43	4.41	4.39	4.43	0.6
Acrylonitrile	5.23	5.23	5.21	5.17	5.14	5.12	5.18	0.9
Tetrachloroethylene	5.66	5.67	5.65	5.60	5.57	5.54	5.62	0.9
1,4-Dioxane	6.58	6.58	6.59	6.50	6.47	6.41	6.52	1.1
Ethylene dichloride	6.92	6.92	6.88	6.82	6.77	6.72	6.84	1.2

[a] The 10 min reconcentration time is subtracted.

[b] Relative standard deviation.

TABLE 18. REPRODUCIBILITY OF AREA INTEGRATIONS

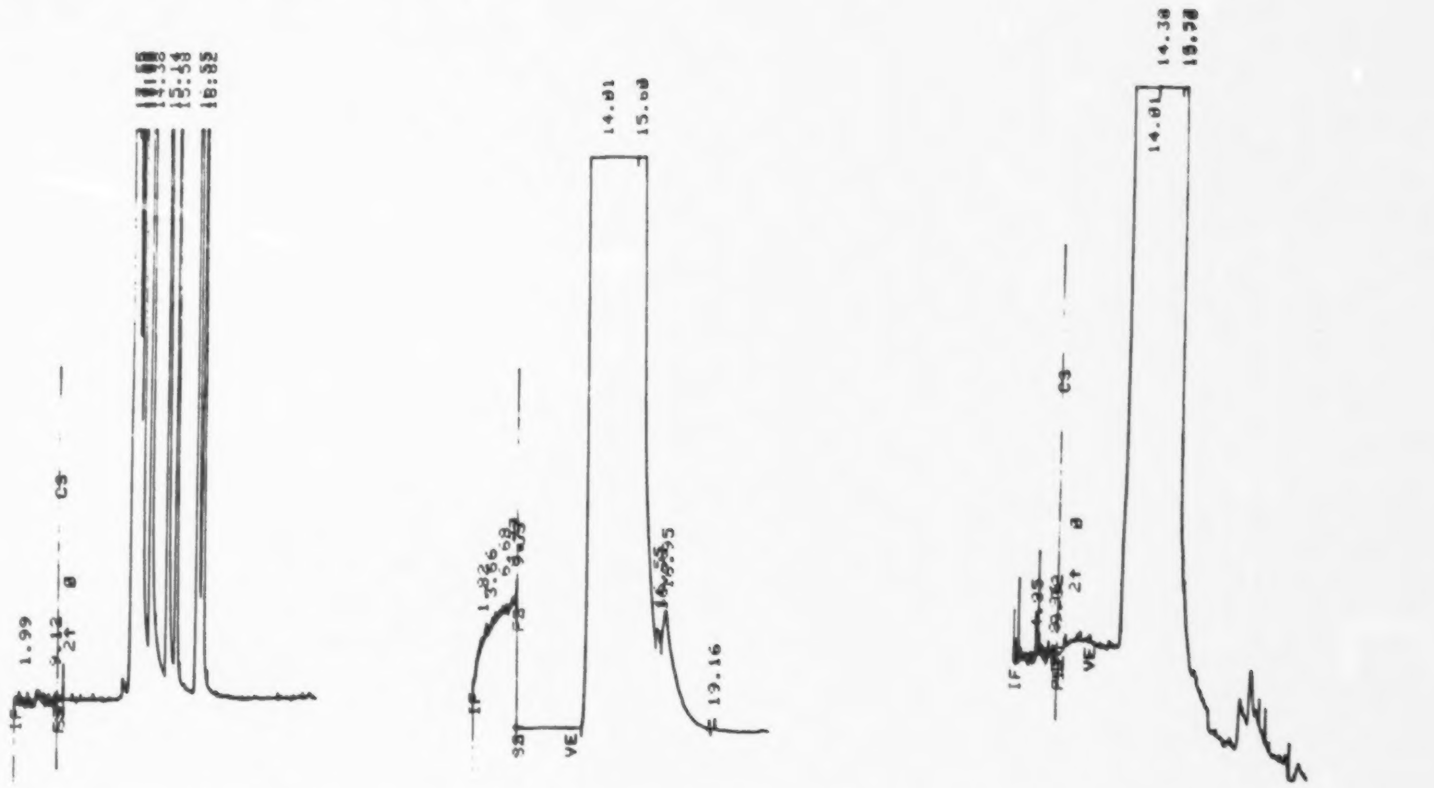
Compound	Area integrated, computer counts						Statistics					
							Corrected for injection size		Corrected for area of solvent		No correction	
	Run #468	Run #469	Run #479	Run #471	Run #472	Run #473	Mean	RSD[a], %	Mean	RSD[a], %	Mean	RSD[a], %
Acetone (solvent)	1,409,000	1,390,000	1,403,000	1,372,000	1,374,000	1,339,000	1,316,163	2.9	-	-	1,381,167	1.8
Acrolein	2,340	2,352	2,277	2,404	2,328	2,378	2,237	4.8	2,380	3.3	2,347	1.9
Carbon tetrachloride	568	552	584	605	576	613	556	5.7	591	5.5	583	3.9
Vinyl acetate	2,360	2,354	2,345	2,272	2,308	2,221	2,201	2.9	2,341	0.8	2,310	2.4
Benzene	7,328	7,236	7,348	7,164	7,168	6,998	6,868	2.8	7,305	0.3	7,207	1.8
Acrylonitrile	2,535	2,469	2,554	3,199	3,220	3,130	2,722	14.7	2,895	14.3	2,851	12.8
Tetrachloroethylene	992	941	966	1,178	1,109	1,055	993	11.3	1,055	9.9	1,040	8.8
1,4-Dioxane	5,577	5,519	5,602	5,444	5,449	5,328	5,228	2.7	5,561	0.3	5,487	1.8
Ethylene dibromide	1,250	1,216	1,307	1,496	1,500	1,332	1,288	11.0	1,370	9.9	1,350	9.0

[a] Relative standard deviation.

solutions. This is demonstrated in Figure 16 for Standard Mixture $(GC)^2$Va (Figure 7). The other problem was the tremendous increase (∿100 fold) in the level of background interferences. Therefore, if instrumental sensitivity is sufficient to permit the detection of compounds in a sample at an acceptable level (0.1 to 10 ng), the "split" mode of injection provides better analytical performance (i.e., fewer interferences) and potential multiple analyses.

RESULTS

The development of the analytical method resulted in an analytical technique which provides major analytical conditions and hardware requirements. This technique allows the separation of most of the twenty selected compounds and permits the introduction of sorbent tube samples obtained by solvent or thermal desorption. An inlet system (Figure 13), shown to efficiently and reproducibly introduce samples into a GC, provides for the introduction of samples thermally desorbed from sorbent tubes. The capillary column found to chromatograph most of the twenty selected compounds adequately (Table 12), to provide a high chromatographic efficiency (Table 15), and to allow rapid, easy installation, was on ∿50 m long, ∿0.2 mm ID, fused-silica, OV-101 WCOT column. A glass WCOT column of the same (OV-101) or equivalent (SP 2100) liquid phase also would probably provide similar chromatographic results, although installation would be more difficult. Fused-silica or glass WCOT columns coated with Carbowax 20 M provided complimentary resolution of compounds (i.e., compounds changed elution order), but did not chromatograph high-boiling compounds. Such polar columns could be used secondarily for multiple sample analyses if further confirmation of compound identities is desired. For any analytical column, a slow temperature-programmed analysis (2 to 3°C/min), from a low temperature (0°C to 35°C) to a temperature ∿30°C below the column temperature limit, provides the best analytical conditions for compound resolution. However, analysis for high-boiling compounds with these analytical conditions is impractically large (213 min for benzo(a)pyrene). Therefore a faster temperature-programming rate (5 to 10°C/min) will probably be required to analyze "field" samples within reasonable time periods (45 to 90 min). At the upper analytical temperature, a column flow rate adjusted to obtain a linear velocity of 17 to 20 cm/sec (with helium carrier) provides optimal conditions for chromatographic efficiency. Injection of a sorbent taken sample with the GC in the "split" injection mode permits recollection of the split portion for multiple analyses and keeps background interferences to a minimum. However, this injection mode reduces analytical sensitivity and its ("split" injection) advantages must be weighed against sensitivity requirements.



A. 200:1 Split of Standard Mixture (GC)^2 Va.

B. Splitless injection of Standard Mixture (GC)^2 Va.

C. Splitless injection of Standard Mixture (GC)^2 Va 100-fold dilution.

Figure 16. Chromatograms of Standard Mixture (GC)^{2}Va comparing split and splitless modes of injection.

In the actual analyses of field samples certain changes were made in the analytical technique owing to either improvement or convenience of operation with the GC/MS system, or conditions/properties of the particular samples (e.g., high water content). These changes are described in detail in Section 10. Most notable among these was the use of splitless injection and capillary direct injection techniques and the modification of the GC temperature program for samples with high water content. The following summarizes the preferred technique used for the analyses:

Instrument: Hewlett-Packard Model 5985B GC/MS

Column: Methyl Silicone (OV101, SE-30, SP2100 or equivalent) capillary (fused silica or glass), 50 m, 0.2-0.25 mm ID.

Temperature Program: Subambient (-30°C) during tube desorption. Rapid rise (∿30°C/min) to 0°C. More gradual temperature rise (∿8°C/min) to ∿30° below upper temperature limit of column.

Inlet System: Nutech Model 320 thermal desorption system, capillary direct coupling.

Mass Spectrometer: Scan Mode

SECTION 8

DEVELOPMENT OF THE SAMPLING SYSTEM

OBJECTIVE

A sampling system was to be developed so that the twenty selected potential carcinogens could be collected effectively for subsequent laboratory analyses. This system was to incorporate a combination of solid sorbents of complimentary adsorption characteristics. As discussed in Section 6, the sorbent materials selected were Tenax-GC, Porapak R, and Ambersorb XE-340. Cartridges containing these sorbents were to be included in a sampling system fabricated for the easy, efficient collection of ambient air samples.

INSTRUMENTATION

The analytical system, described in Section 7, was developed concurrently with the development and evaluation of the sampling technique. This analytical system was used in a variety of configurations (particularly with various capillary columns) for the analyses of sorbent cartridges. The analyses of the sorbent cartridge were measured against analytical standards to allow the comparison of results obtained with the various analytical configurations. Vaporous samples of the more volatile compounds of interest were produced with the Sample Generation System described in Appendix B. These samples were "known" artificial atmospheric environments which could be sampled with sorbent cartridges. This allowed the evaluation of the sorbent cartridges under somewhat realistic sampling conditions.

EVALUATION

Design Criteria

The first step in the development of the ambient air collection system was to evaluate the basic design options and criteria of an air sampling system. The most basic sorbent sampling system (Figure 17) is comprised of only four major elements: a particulate filter, usually placed at the inlet of a system; a cartridge to contain the sorbent material; a pump to draw the air sample; and, tubing to connect the filter, cartridge, and pump. However, specific parameters such as flow rate, cartridge design,

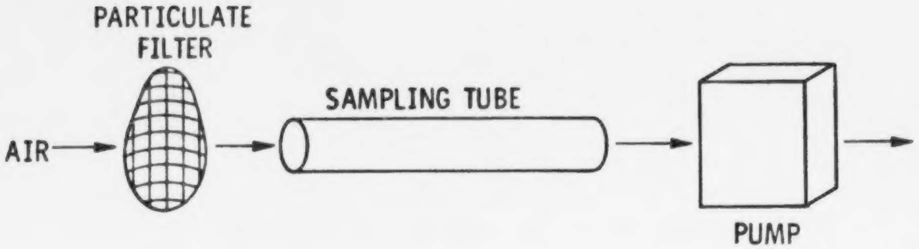


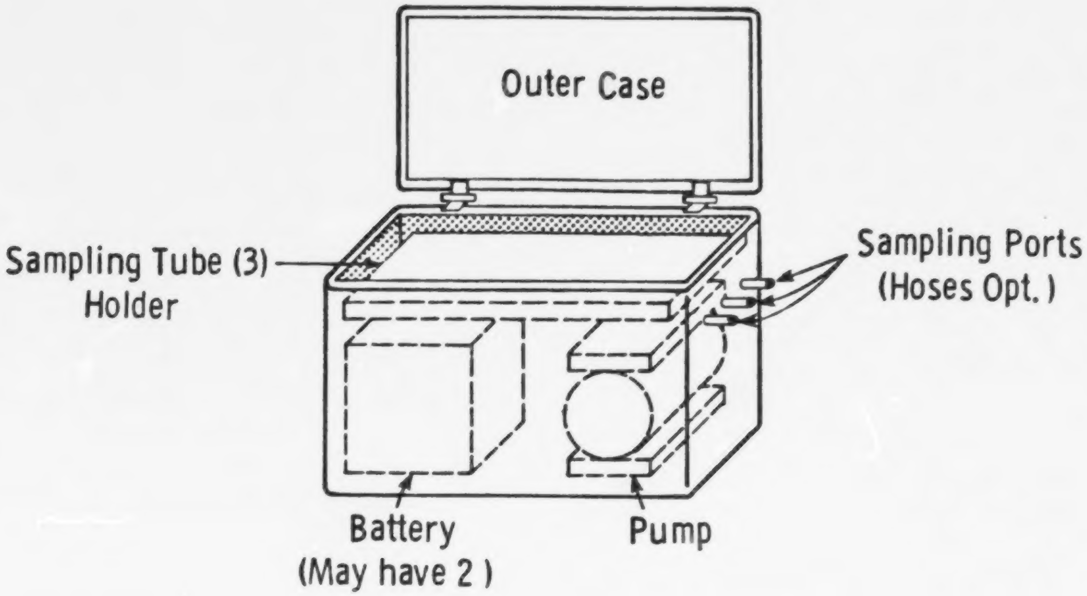
Figure 17. Basic sampling system.

and materials of construction need to be adapted to the specific sampling application. Therefore, these four basic elements and various sampling parameters were assessed with respect to this project.

Since some of the compounds of interest, such as acrylonitrile and benzyl chloride, tended to be reactive, inert materials were chosen for the fabrication of the sampling system. Silanized pyrex glass was the material selected for the sorbent cartridges. Similarly, silanized pyrex glass wool was chosen for containing the sorbents within cartridges and for use as a particulate filter. Interconnecting tubing was preferably inert, flexible, and non-contaminating, so Teflon was selected as the most suitable material. Stainless steel was chosen for connecting fittings.

Another area of consideration was the size, weight, cost, and durability of the sampling system versus the sampling capabilities of the pump. Since a portable system was being developed under EPA Contract 68-02-2774, a larger system was desired for this contract. The desk-top type of sampling system, shown in Figure 18, was selected for investigation. This system would be an area-monitoring (versus personal-monitoring) sampling system, portable enough to be hand-carried to field locations without heavy equipment. In comparison to the portable system developed for the other contract, this system would be more durable and be capable of sampling at higher flow rates. The size and weight would be greater but the cost would be approximately the same as the portable system. Although a large vacuum pump could be placed in such a system, a more moderately sized pump was thought to be potentially more suitable, especially because of weight considerations. The sampling capabilities of two pumps considered are shown in Figure 19.

Combining the three selected sorbent materials within a single sampling system also had to be contemplated. In a previous application for the collection of jet exhaust fumes, different


Outer Case
Sampling Tube (3) Holder
Sampling Ports (Hoses Opt.)
Battery (May have 2)
Pump

WEIGHT	∿32 lbs (∿60 if 2 batteries)
COST	∿$385 (for case, 1 battery, charger and pump only)
SIZE	13" (long) x 8" (wide) x 5" (deep)
OPERATION TIME	4-6 hrs (>8 hrs with 2 batteries or wall adaptor)[a]
METHOD OF SETTING FLOW	Needle valves and flow meters or critical orifices[b]
DURABILITY PROBLEMS	Needle valves (if used) fragile

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[a] Battery may be put into a separate pack and/or a 120V line with transformer may be used to adapt this sampler to a wall socket.

[b] Due to pressure drop required at orifices the capabilities would be reduced.

Figure 18. Sketch and description of large desk-top sampler.

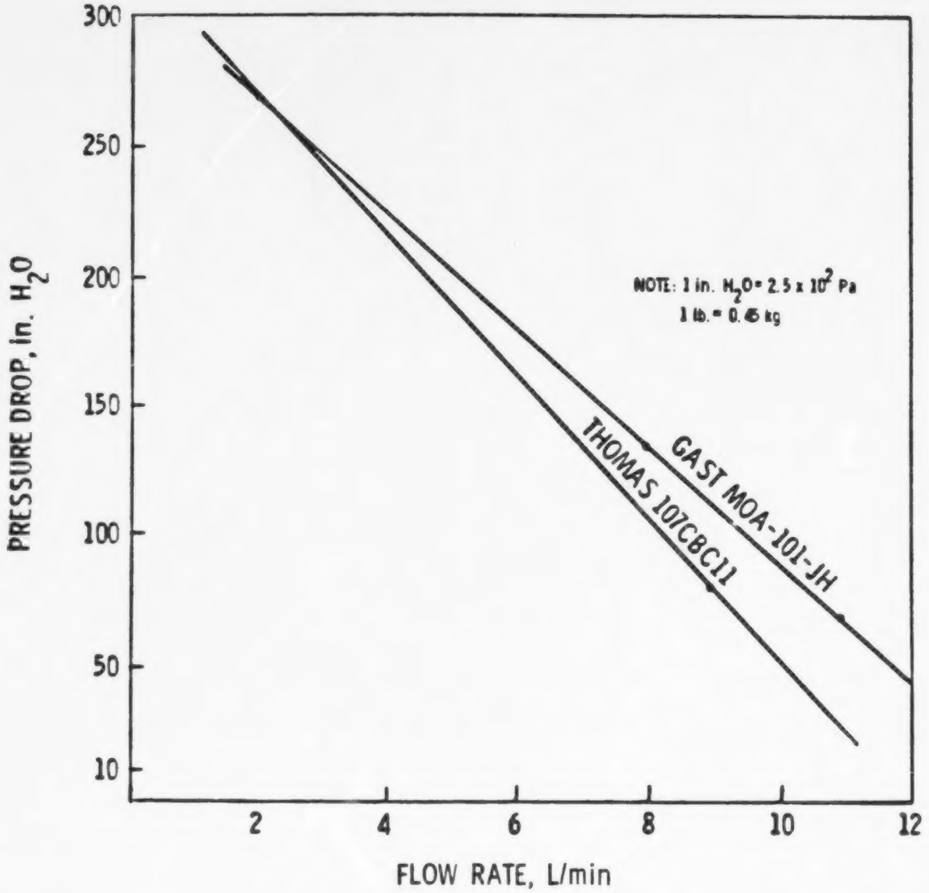

Figure 19. Plots of requirements for various sampling arrangements and the manufacturer's specifications for two large (desk-top) pumps.

sorbents were combined within a single cartridge [49]. However, the three sorbents selected for this application did not have compatible temperature limits. The temperature limit of Porapak R (250°C) is significantly less than Tenax-GC (350°C) and Ambersorb XE-340 (>400°C). Therefore, if thermal desorption was used to analyze these tubes, a low temperature would be required for sorbents combined in a single cartridge, or optimal desorption temperatures would be possible for sorbents in separate cartridges. The latter arrangement was chosen for investigation. The separation of sorbents into different sorbent cartridges allows the additional option of parallel or series sampling. Table 19 qualitatively describes the performance of the three sorbent materials anticipated for these two sampling modes. It assumes the δ_m range (for the sorbent cartridges given in Table 9 (in Section 6) which was based on ∿1 g per sorbent and a sample volume of 480 L. An evaluation of the two sampling modes was to be performed during laboratory development of the sampling system.

The relationship of atmospheric concentration, analytical detection limit, sample volumes, and sorbent capacities was investigated with respect to sampling limitations. Concentration and detection of organic compounds at atmospheric concentrations of ∿1 to ∿10 parts per trillion (ppt)[a] was set as an objective. Assuming an analytical detection limit of 10 ng, Figure 20 shows the relationship between atmospheric concentration and sample volume necessary to collect a detectable sample of benzene. The larger the volume of sample collected, the lower the atmospheric concentration which is detectable. However, there are limitations to the amount of sample that can be collected on sorbent materials. One limitation is the capacity of a sorbent or sorbent system for any particular compound. The capacities per gram of sorbent of Tenax-GC, Porapak R, and Ambersorb XE-340 for benzene are also shown in Figure 20. As indicated, if a sample is collected at a rate of 3 L/min for 8 hours, the capacities of 1 gram of Tenax and Porapak R for benzene would be exceeded. Benzene would "break through" sorbent cartridges containing 1 g of these sorbents before being concentrated to an analytically detectable level. However, the capacity of 1 g of Ambersorb XE-340 for benzene is much greater than the sample volume indicated. By collecting that sample volume, atmospheric concentrations of benzene could be detected down to ∿2 ppt with an Ambersorb cartridge. Similar relationships

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[a] $1 \text{ ppt} \times \frac{MW}{24450} = 1 \text{ ng/L}$ (in air at STP)

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[49] Brooks, J. J., D. S. West, J. E. Strobel, and L. Stamper. Jet Exhaust Analysis by Subtractive Chromatography. SAM-TR-78-37, USAF School of Aerospace Medicine, Brooks Air Force Base, Texas, Dec. 1978. 76 pp.

TABLE 19. EVALUATION OF SORBENT PACKAGE FOR TWO MODES

Sorbent	Mode			
	Series		Parallel	
	Trap	Desorb	Trap	Desorb
Tenax-GC (δ_m, ~950 to >2,800)	Quantitatively trap all low and some intermediately volatile compounds and partially (<100%) trap all other compounds.	Quantitatively desorb (almost) all compounds trapped, including those only partially trapped.	Quantitatively trap all low and some intermediately volatile compounds, and partially (<100%) trap all other compounds.	Quantitatively desorb (almost) all compounds trapped, including those only partially trapped.
Porapak R (δ_m, ~750 to ~1,500)	Quantitatively trap all intermediately volatile compounds passing through the Tenax, and partially (<100%) trap all other compounds passing through Tenax.	Quantitatively desorb all compounds trapped from Tenax breakthrough, including those only partially (<100%) trapped.	Quantitatively trap all low and intermediately volatile compounds, and partially (<100%) trap all other compounds.	Quantitatively desorb most of the intermediately volatile and partially trapped compounds, and partially (<100%) desorb some intermediately and low volatility compounds.
Ambersorb XE-340 (δ_m, ~450 to ~750)	Quantitatively trap most of the highly volatile compounds breaking through both the Tenax and the Porapak with other more volatile compounds being partially (<100%) trapped.	Quantitatively desorb most of the compounds trapped, except possibly those highly volatile compounds that border on intermediate volatility which may only partially (<100%) desorb.	Quantitatively trap all of the low and intermediately volatile compounds and most of the highly volatile compounds and partially (<100%) trap even more highly volatile compounds.	Quantitatively desorb most of the highly volatile quantitatively and partially trapped compounds, partially desorb (<100%) some intermediately (and border) volatile compounds, and not desorb (~0%) most other compounds.

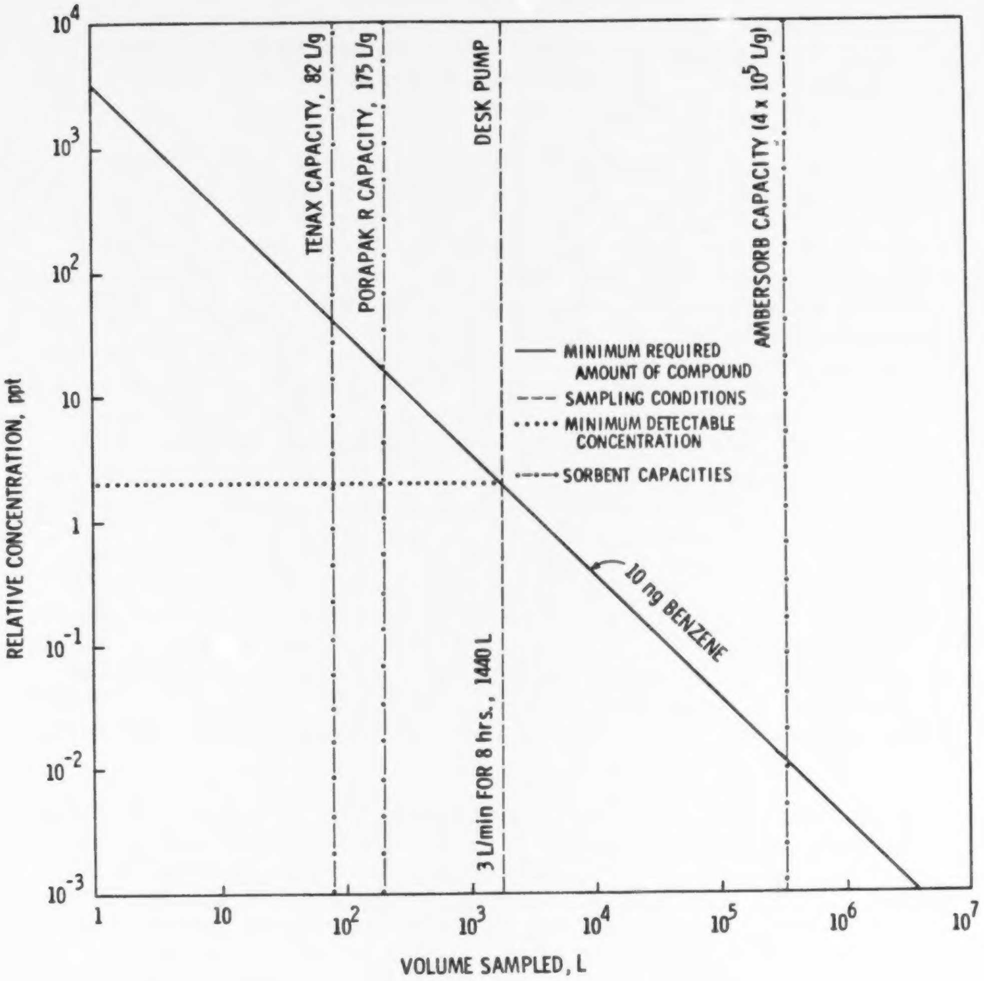


Figure 20. Relationship between concentration, volume sampled, and approximate detection limit (10 ng) for benzene with sorbent capacities superimposed (assuming 1 gram of sorbent).

between sorbent capacity, atmospheric concentration, sample volume, and analytical detection limit exist for all atmospheric pollutants. Thus, for any given sample volume, different groups of atmospheric pollutants will be concentrated to analytically detectable levels on different sorbent materials. The lowest detectable atmospheric concentration of any particular pollutant is determined by the sample volume, as long as that volume doesn't exceed the collecting sorbent's capacity for that pollutant.

Theoretically, one could decrease the detectable atmospheric concentration of a pollutant to an infinitely small level by greatly increasing the sample volume, as long as the amount of sorbent is increased to quantitatively collect the pollutant with that larger sample volume. However, there are practical, physical limitations to this approach. The major limitation is the sampling capabilities of pumps. For any pump there are limits to the flow rate capable of being drawn over a given pressure drop, as indicated in Figure 19. For a given period of time, the sample volume capable of being drawn by a pump is directly related to the pressure drop across the system in which it is incorporated. For sorbent cartridges, the pressure drop across a single cartridge is determined by the amount, type, and mesh size of the sorbent material, the diameter of the tube, the type and amount of material (e.g., glass wool) used to contain the sorbent, and the flow rate through the tubes. For a multiple cartridge system, series or parallel arrangement of cartridges, interconnecting tubing, and any flow controlling valves also add to the pressure drop across a system. Therefore, minimum detectable atmospheric concentrations of pollutants are limited by both sorbent capacity and the physical design of a sampling system.

The physical design of the sampling system for this project was developed so that sorbent capacities were maximized and pressure drops minimized (thereby allowing any pump to draw a maximum sample volume). The first step was to select a cartridge design for the three chosen sorbent materials which would potentially allow the efficient collection of the twenty selected potential carcinogens. Under EPA Contract 68-02-2774, pressure drop studies were conducted with a variety of sorbent tube designs [47]. The tube design depicted in Figure 21 was selected as offering a reasonable compromise between the requirement to have the smallest possible diameter for efficient thermal desorption (theoretically more sensitive than solvent desorption) and an acceptable pressure drop. With this design, glass cartridges could contain $\sim$1 g of Tenax, $\sim$1.5 g of Porapak R and $\sim$3 g of Ambersorb. The abilities of these sorbent cartridges to collect the twenty compounds of interest was estimated by determining the molecular weight modified solubility parameters (δ_m) of the twenty selected compounds. These compounds were arranged with the test matrix compounds (previously discussed in Section 6) according to

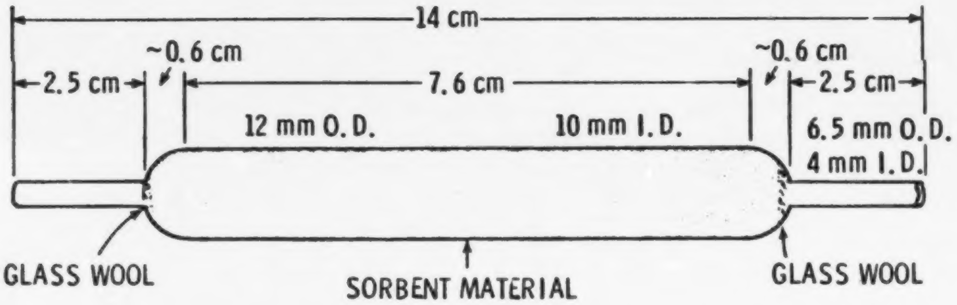


Figure 21. Specifications of selected sampling tube design.

increasing δ_m value. The abilities of the sorbent cartridges to collect and desorb these compounds were qualitatively evaluated for a sample volume of ∿1,500 L. The results of these evaluations are summarized in Table 20. The enclosed regions indicate compounds anticipated to be quantitatively collected and desorbed with these cartridges using this sample volume. As indicated, all of the twenty compounds of interest theoretically are effectively sampled with sorbent cartridges of this design. Therefore, this sorbent cartridge design (Figure 21) was tentatively selected for use in the Ambient Air Collection System pending laboratory evaluation.

Sorbent Cartridges

Conditioning--

Generally, all commercially available sorbent materials, including the three selected for this project, contain significant levels of background contamination upon receipt as the result of production, packaging, and/or transportation. Cleanup procedures for sorbents range from short (∿1 hr) thermal conditioning to exhaustive conditioning techniques involving extraction with multiple solvents and rigorous (>8 hr) thermal conditioning [46]. Since the sorbent cartridges for this project were to collect ambient air samples containing trace levels of organic compounds, an exhaustive cleanup procedure was selected. This procedure is described in Appendix C. "Blank" sorbent cartridges prepared according to these procedures and analyzed with the analytical system described in Section 7 were found to have acceptable backgrounds, as demonstrated by the chromatograms in Figure 22.

Capacity--

The ability of the sorbent cartridge to retain some of the compounds of interest was briefly investigated. As discussed in Section 6, a chromatographic technique was used to estimate sorbent capacities (Table 7 in Section 6) which were then related

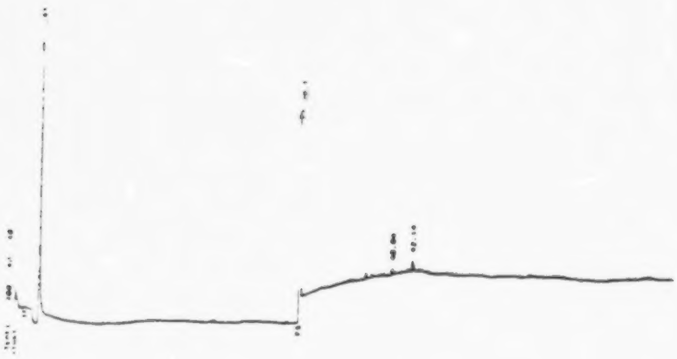
TABLE 20. SUMMARY OF ANTICIPATED SAMPLING CHARACTERISTICS AND CAPABILITIES

General information				Sorbent ranges of utility					
				Tenax		Por. R		Amb. 340	
Name of compound	δm	MW	BP, °C	Trap	Desorb	Trap	Desorb	Trap	Desorb
Methane	89	16.04	-164	0	/	0	/	0	/
Ethane	180	30.07	-88.63	0	/	0	/	0	/
Propane	282	44.09	-42.07	0	/	0	/	0	/
n-Butane	395	58.12	-0.5	0	/	0	/	0	/
Ethylene oxide[a]	489	44.05	10.7	0	/	0	/	√?	X?
n-Pentane	505	72.15	36.07	0	/	0	/	√	X?
Propylene oxide	534	58.08	34.3	0	/	0	/	√	X?
Acrylonitrile	557	53.06	78.9	0	/	0	/	√	X?
Acrolein	560[b]	56.06	52.5	0	/	0	/	√	X?
n-Hexane	629	86.17	69.0	0	/	0	/	√	X?
Benzene	719	78.11	80.1	0	/	0	/	√	X?
Vinyl acetate	769[b]	86.09	72.2	0	/	√?	/	√	X?
iso-Octane	788	114.22	99.3	0	/	√	/	√	X?
Ethylene dichloride	806	98.96	83.47	0	/	√	/	√	X?
1,4-Dioxane	881	88.10	101.5	0	/	√	/	√	X?
Ethylene glycol	906	62.07	197.2	0	/	√	X?	√	X?
Ethylene dibromide	946	187.87	131.36	√?	/	√	X?	√	X?
Styrene	969	104.14	146	√?	/	√	X?	√	X?
Succinonitrile	1,073[b]	80.09	267	√	/	√	X?	√	X
Phenol	1,176	94.11	182	√	/	√	X?	√	X
Benzyl chloride	1,253	126.58	179	√	/	√	X?	√	X
Naphthalene	1,269	128.16	217.9	√	/	√	X?	√	X
Carbon tetrachloride	1,323	153.84	76.8	√	/	√	X?	√	X
Bis-(2-chloroethyl) ether	1,402	143.02	178	√	/	√	X?	√	X
Tetrachloroethylene	1,542	165.85	121.02	√	/	√	X?	√	X
Toluene-2,4-diamine	?	122.17	280	√	/	√	X?	√	X
o-Nitroaniline	1,657[b]	138.12	284.11	√	/	√	X	√	X
m-Nitroanisole	1,684[b]	153.13	258	√	/	√	X	√	X
Phenanthrene	1,747	178.22	340.2	√	/	√	X	√	X
n-Hexadecane	1,811	226.43	287.5	√	/	√	X	√	X
1,2,4-Trichlorobenzene	2,014[b]	181.46	213	√	/	√	X	√	X
Benzidine	?	184.2	401.7(s)	√	/	√	X	√	X
4-Bromodiphenyl ether	2,616[b]	249.11	310.14	√	/	√	X	√	X
Pentachlorophenol	?	266.35	310(d)	√	/	√	X	√	X
Hexachloro-1,3-butadiene	2,783[b]	267.6	215	√	/	√	X	√	X
Di-(2-ethylhexyl) phthalate	?	?	385	√	X?	√	X	√	X
Chrysene	?	228.3	498	√	X?	√	X	√	X
Benzo(a)pyrene	?	252.3	?	√	X?	√	X	√	X

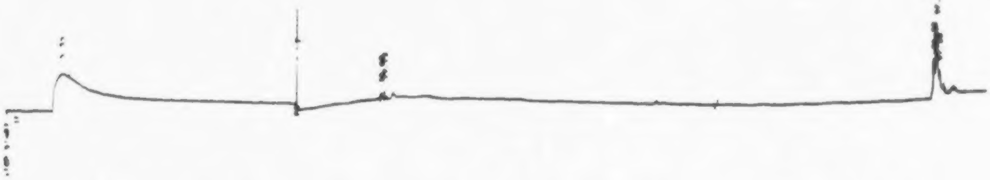
[a] Underlined words are the 20 selected possible and probable carcinogens.

[b] δ_m from calculated δ.

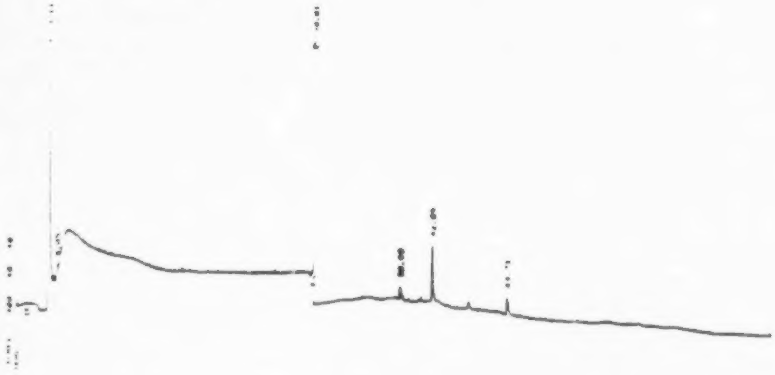
KEY:
- 0 - Probable trap breakthrough.
- √? - Possible trap breakthrough.
- √ - Quantitative trapping (with appropriate amount of sorbent).
- / - Quantitative desorption.
- X? - Possibly not desorbed.
- X - Probably not desirbed.
- s - Sublimed.
- d - Decomposes.



A. Analysis of a blank Tenax-GC sorbent tube.



B. Analysis of a blank Porapak R sorbent tube.



C. Analysis of a blank Ambersorb XE-340 sorbent tube.

Figure 22. Backgrounds produced by desorbing blank sorbent tubes.

to the parameter δ_m. This chromatographic technique is known as the "elution" method of sorbent capacity determination. Another technique of sorbent capacity determination which more realistically approximates sorbent sampling conditions is 'frontal analysis". By this technique a sorbent cartridge is exposed to a given (challenge) concentration of a single compound and its effluent monitored for breakthrough. Figure 23 depicts a comparison of the two techniques. Using the Sample Generation System (Appendix B). "frontal analyses" were performed on the three types of sorbent cartridges with benzene, carbon tetrachloride, and acrylonitrile. These results are compiled in Table 21 and compared to their estimated values. Generally the "frontal analyses" showed the sorbent cartridges' capacities to be less than those estimated. though usually in the same order of magnitude (except for carbon tetrachloride). "Breakthrough" of the challenge compounds from the Ambersorb cartridges was very difficult to detect because slow "breakthrough" was indistinguishable from baseline drift. Based on these studies, the anticipated retention capabilities of the sorbent cartridges shown in Table 20 was judged to be plausibly realistic. The analyses of backup tubes during the collection of actual field samples was thought to be the best means of demonstrating the collection capabilities of the selected sorbent cartridges, since matrix effects could greatly alter sorbent capacities.

Desorption Properties--
After a sample has been collected and concentrated on a sorbent tube, two major techniques, thermal and solvent desorption exist for recovering the sample from the tube for analysis. In thermal desorption, a sorbent tube containing a sample is heated to a temperature high enough to volatilize the sample, such that a stream of carrier gas flowing through the sorbent will cause the sample to quickly migrate from the tube into an analytical system. The capillary inlet system, discussed previously, was designed for the thermal desorption of sorbent cartridges. With solvent desorption, the sample is recovered from the sorbent tube by extracting the sorbent with an appropriate solvent. The resulting solution is then introduced into an analytical system by syringe injection.

Thermal and solvent desorption have differing advantages. For example, solvent desorption permits numerous replicate analyses, but the solvent dilutes the sample of interest (often >1000 fold). This defeats at least some of the sample concentration accomplished by sorbent sampling and reduces overall method sensitivity. On the other hand, thermal desorption can achieve a maximum sensitivity by introducing all of a collected sample into an analytical system; however, this does not permit replicate analyses. By splitting a thermally desorbed sample, replicate analyses can be performed but sensitivity is decreased by the amount of the split.

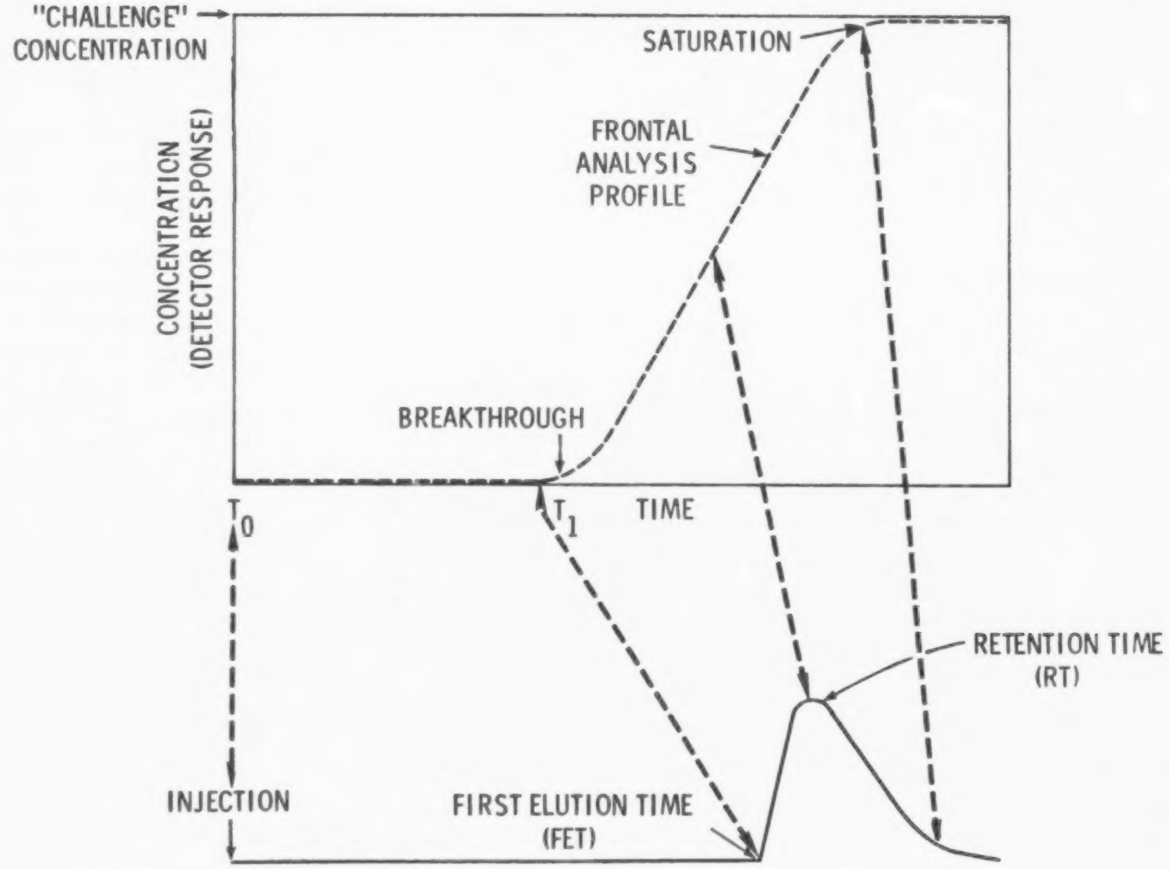

"CHALLENGE"
CONCENTRATION
CONCENTRATION (DETECTOR RESPONSE)
SATURATION
FRONTAL ANALYSIS PROFILE
BREAKTHROUGH
T_0
T_1
TIME
RETENTION TIME (RT)
INJECTION
FIRST ELUTION TIME (FET)

Figure 23. Comparison of "frontal" and "elution" methods of sorbent capacity determination.

TABLE 21. RESULTS OF FRONTAL ANALYSES OF SORBENT TUBES

							Frontal analyses information						
			Sampling parameters				Breakthrough			Saturation		Total exposure	
Compound	Sorbent	Weight, g	Rate, L/min	Temp., °C	Pressure, atm	"Elution" capacity estimate @20°C	Time, min	Amount, µg	Volumetric capacity, L/g	Time, min	Amount, µg	Time, min	Amount, µg
Carbon tetra-chloride	Tenax-GC	0.9	$\sim$1.025	$\sim$25	$\sim$1	$>1.02 \times 10^{4}$ [a]	<0.5	<3.6	<0.57	$\sim$3	$\sim$21	$\sim$13	$\sim$92
	Porapak R	1.5	$\sim$0.886	$\sim$25	$\sim$1	$>6.6 \times 10^{5}$ [a]	$\sim$30	$\sim$184	$\sim$18	- [b]	-	$\sim$51	$\sim$313
	Ambersorb XE-340	3.2	$\sim$0.975	$\sim$25	$\sim$1	$>4.0 \times 10^{5}$ [c]	- [d]	-	-	-	-	$\sim$420	$\sim$2,840
Benzene	Tenax-GC	0.9	$\sim$0.979	$\sim$25	$\sim$1	82 [e]	$\sim$8	$\sim$30	$\sim$8.7	- [b]	-	$\sim$39	$\sim$147
	Porapak R	1.5	-	-		175 [e]	- [f]	-	-	-	-	0	0
	Ambersorb XE-340	3.2	-	-	-	$>4.0 \times 10^{5}$ [g]	- [f]	-	-	-	-	0	0
Acrylo-nitrile	Tenax-GC	0.9	$\sim$1	$\sim$25	$\sim$1	8.4 [e]	2.5	8.5	$\sim$3	>7.5	$\sim$26	$\sim$24	$\sim$21
	Porapak R	1.5	$\sim$1	$\sim$25	$\sim$1	25.2 [e]	$\sim$13	$\sim$44	$\sim$9	27.5	$\sim$94	$\sim$38	$\sim$128
	Ambersorb XE-340	3.2	$\sim$1	$\sim$25	$\sim$1	>24,000 [h]	- [i]	-	>206	-	-	$\sim$660	$\sim$2,250

[a] Based on the fact that δ_m for carbon tetrachloride is greater than δ_m for benzyl chloride.

[b] Exposure discontinued before saturation obtained.

[c] Based on the fact that δ_m for carbon tetrachloride is greater than δ_m for n-hexane.

[d] Results were inconclusive.

[e] Previously determined.

[f] Not completed.

[g] Based on the fact that δ_m for benzene is greater than δ_m for n-hexane.

[h] Based on the fact that δ_m for acrylonitrile is greater than δ_m for n-pentane.

[i] Exposure discontinued before breakthrough obtained.

A brief study was conducted to compare thermal and solvent desorption. Two solvent desorption techniques, shown in Figures 24 and 25, were compared to thermal desorption of benzene from Ambersorb XE-340 cartridges. The benzene samples were generated with the Sample Generation System (Appendix B) and compared to analytical standards. A sample of benzene was also thermally descrbed from a Porapak R cartridge for comparison. The recoveries obtained, based on the theoretical amount of benzene generated, are given in Table 22. Assuming the actual amount of benzene generated was somewhat higher than the theoretical amount, more efficient recovery was indicated by thermal desorption. In another experiment, some laboratory air samples were collected with the sorbent cartridges and then analyzed. One Ambersorb XE-340 tube was solvent desorbed with little detected during its analysis. A similar Ambersorb XE-340 sample that was thermally desorbed yielded a much more complex chromatogram, demonstrating the superior sensitivity attainable by thermal desorption. Therefore, thermal desorption was selected as the most suitable sample recovery technique.

TABLE 22. EVALUATION OF THE DESORPTION EFFICIENCY OF BENZENE FROM AMBERSORB XE-340

Sample	Theoretical amount, μg	Amount recovered, μg	Percent recovery
First wash of benzene exposed Ambersorb tube	0.90	0.76	84
Second wash of benzene exposed Ambersorb tube	∿0	0.01	(1.2)[b]
Ambersorb tube emptied in acetone bath	0.90	0.59	66
Benzene exposed Porapak R tube thermally desorbed	∿5.7[c]	7.9	138
Benzene exposed Ambersorb tube thermally desorbed	0.86	1.38	160

[a] The amount theoretically contained within the sample.

[b] The percentage of the first wash of that tube.

[c] Sampling rate and time were inaccurate, so that the actual amount of the sample may be higher than that indicated.

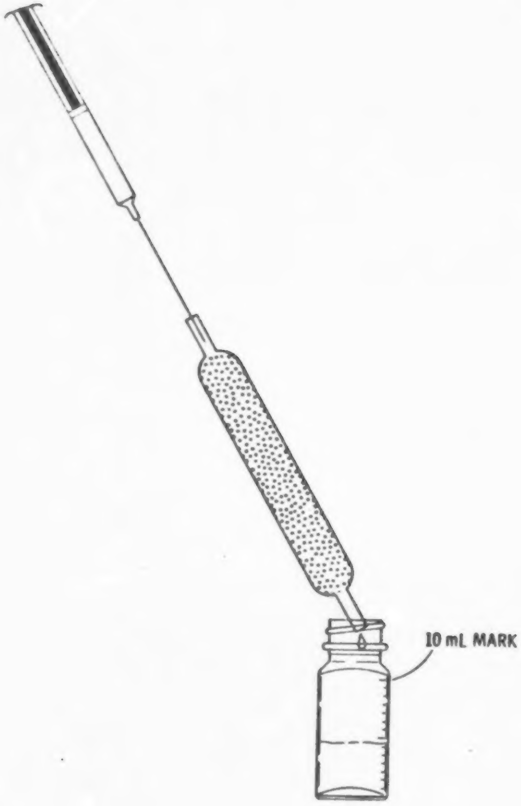
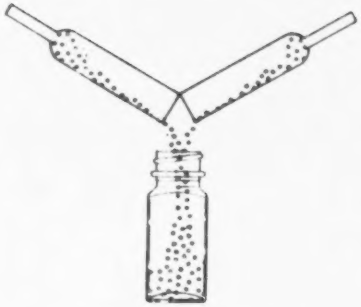
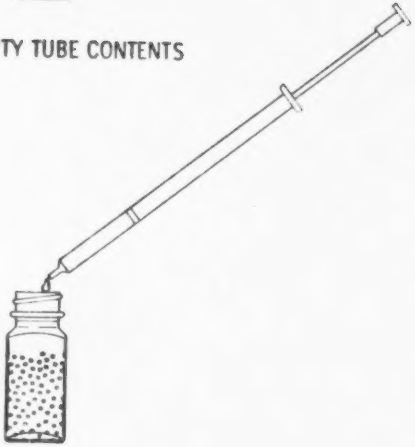


Figure 24. "Pass-through" solvent desorption technique.



A. EMPTY TUBE CONTENTS



B. ADD SOLVENT

Figure 25. Solvent "bath" desorption technique.

Two methods were used to determine the efficiency of recovering some of the twenty selected compounds from the sorbent cartridges by thermal desorption. One technique was to inject analytical standards through a septum tee (Figure 15, Section 7) into a sorbent cartridge enclosed by the capillary inlet system desorption chamber. The sample was then desorbed through the entire sorbent cartridge into the analytical system. The recoveries summarized in Table 23 were obtained by comparing results of standards desorbed through sorbent cartridges to results of standards desorbed through an empty glass cartridge. The other method was to collect a vaporous compound mixture made with the Sample Generation System on sorbent cartridges and thermally desorb these cartridges. The results were quantitated by comparison to analytical standards and these values compared to the theoretical amounts collected from the Sample Generation System. The recoveries obtained are compiled in Table 24. Assuming the actual concentrations of the generated compounds were somewhat different than their theoretical concentrations, certain recovered amounts were selected as representing true values. The recoveries obtained from various sorbent tubes could then be compared to each other as given in Table 25. These recovery experiments demonstrated that most of the compounds evaluated were efficiently desorbed from the Tenax and Porapak R sorbent cartridges; however, recoveries of compounds from Ambersorb XE-340 cartridges were biased in favor of the less polar compounds. If these sorbent cartridge are combined in series with the Ambersorb tube last, most high-molecular weight and polar compounds should be adsorbed on the Tenax and Porapak R tubes. Therefore, most compounds not efficiently desorbed from Ambersorb should be retained on the sorbent tubes prior to it.

TABLE 23. RECOVERY OF STANDARDS FROM SORBENT TUBES

	Sorbent material[a]		
Compound	Tenax	Porapak R	Ambersorb
Carbon tetrachloride	79	101	10
Vinyl acetate	105	107	-[b]
Benzene	109	102	81
Tetrachloroethylene	110	91	51
Ethylene dichloride	108	104	15
1,4-Dioxane	105	100	-[b]
Ethylene dibromide	129	90	-[b]
Styrene	106	-[c]	-[c]
Hexachloro-1,3-butadiene	108	-[c]	-[c]
Benzyl chloride	59	-[c]	-[c]

[a] Values under sorbents are percentages found versus theoretical amounts.

[b] No peak of similar retention time observed.

[c] Not evaluated.

TABLE 24. PERCENT RECOVERIES OF THEORETICAL AMOUNTS OF GENERATED SAMPLES

		Compound[a]									
Tube #	Tube Type	Acrolein	Carbon tetra-chloride	Vinyl acetate	Ben-zene	Acrylo-nitrile	Tetra-chloro-ethylene	Dioxane	Ethylene di-chloride	Average % of theoretical amount	R.S.D. of theoretical percentages, %
18	Porapak R	20	84	81	126	47	47	42	180	78	67
67	Porapak R[b]	50	78	57	77	17	27	25	105	54	57
54	Ambersorb	11	17	18	143	52	23	20	124	51	103
119	Tenax-GC	41	212	72	66	38	69	39	78	77	74

[a] Values under compounds are the percentages found versus the theoretical amounts.

[b] Analyzed one week after tube #18.

TABLE 25. PERCENT RECOVERIES OF SELECTED AMOUNTS OF GENERATED SAMPLES

		Compound[a]									
Tube #	Tube Type	Acrolein	Carbon tetra-chloride	Vinyl acetate	Ben-zene	Acrylo-nitrile	Tetra-chloro-ethylene	Dioxane	Ethylene di-chloride	Average % of selected amount	R.S.D. of percentages, %
18	Porapak R	39	100[b]	100[b]	100[b]	100[b]	100[b]	100[b]	100[b]	92	23
67	Porapak R[c]	100[b]	93	71	61	37	58	60	58	67	30
54	Ambersorb	21	20	22	113	112	48	48	69	57	68
119	Tenax-GC	83	253	89	52	82	148	93	43	105	64

[a] Values under compounds are the percentages found versus the selected amounts.

[b] Selected amount -100% by definition.

[c] Analyzed one week after tube #18.

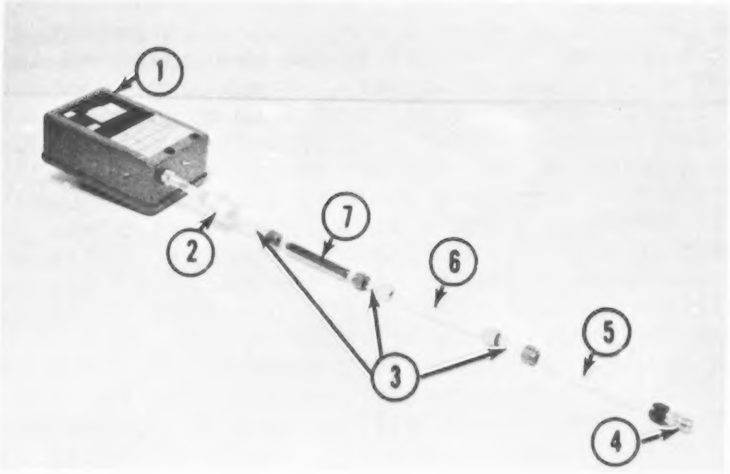
As mentioned previously, the cartridge design given in Figure 21 was selected as potentially offering both acceptable thermal recoveries and an acceptable pressure drop, while containing sufficient sorbent to collect the compounds of interest (Table 20). Increasing the diameter of the cartridge or the amount of sorbent in the cartridge would further decrease the ability to thermally desorb compounds from the sorbent cartridges. Furthermore, solvent desorption results in an unacceptable decrease in method sensitivity. Therefore, the cartridge design shown in Figure 21 was selected for use in the Ambient Air Collection System.

Sampling System

The ability of a pump to draw air through the selected sorbent cartridges in parallel or series modes was compared under EPA Contract 68-02-2774. For this work, a small personal pump was attached to "breadboarded" configurations of sampling systems in the two sampling modes. These configurations are shown in the photograph in Figure 26 and the schematic in Figure 27. A comparison of these two sampling configurations demonstrated that with the small personal pump a flow rate of ∿1 L/min per tube could be attained with the series arrangement, while only ∿0.5 L/min per tube could be attained with the parallel arrangement. The reduced flow rate attained in the parallel configuration was attributed largely to the metering valves used to adjust the flows through the different sorbent cartridges. The valves, rotometers and other additional parts required for the parallel sampling arrangement would result in a sampling system with greater cost, weight, and complexity, and less accuracy, durability, and flow capability. Furthermore, the series configuration would have the additional advantage of fractionating compounds in air samples into zones of different volatilities on the different sorbent cartridges, thereby aiding the subsequent chromatographic separation of the complex samples. Therefore, the series arrangement was selected as the more suitable for the Ambient Air Collection System.

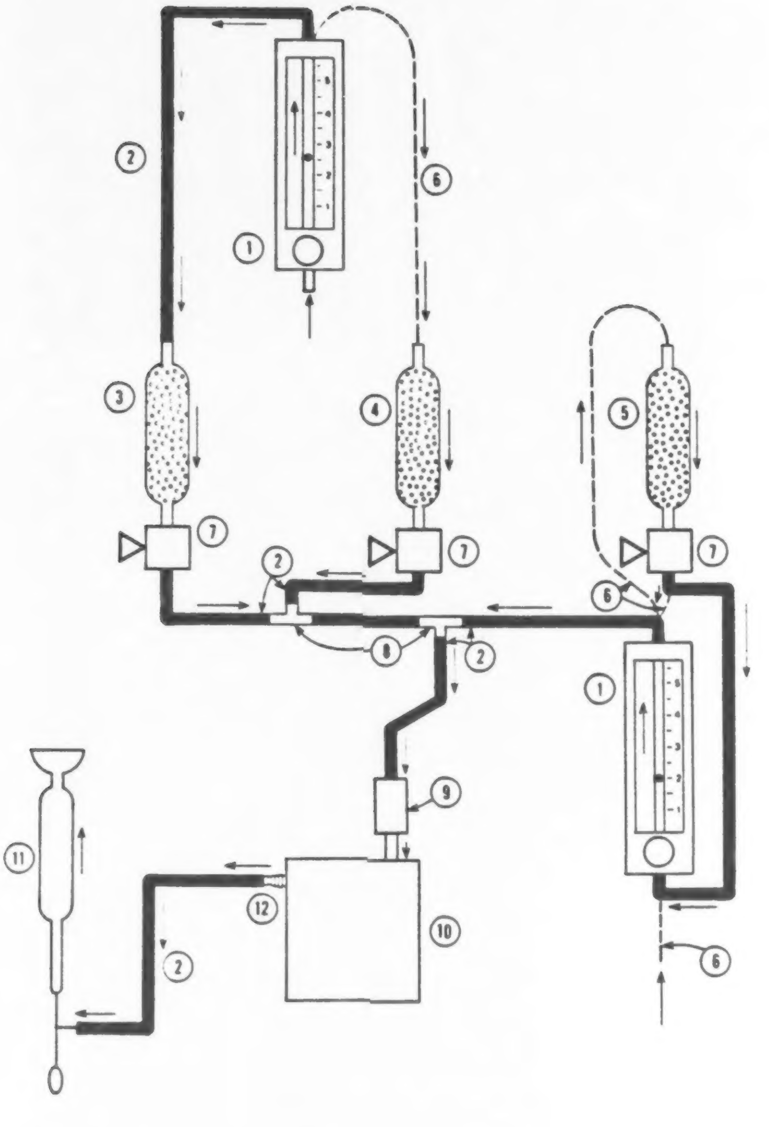
For convenience, a tray was designed to contain the sorbent cartridges during sampling. The specifications of this sorbent tube tray and the procedure of "loading" it are given in the Operation Manual for the Ambient Air Collection System (Appendix C). Figure 28 shows a "loaded" sorbent tube tray ready for sample collection.

A commercially available, gas sampling device was obtained for use in the Ambient Air Collection System. This device, a Nutech Model 221 Gas Sampler, contained a pump of the type thought to be most applicable for this project (see Figure 19). It also included a valve and rotameter for monitoring and adjusting the flow rate, a dry gas meter to measure the pressure drop across which the pump was drawing, and power adaptability to either an AC (outlet) or DC (battery) supply. (A power supply



1 - DUPONT P4000 PUMP
2 - PUMP PRE-FILTER
3 - TYGON TUBING
4 - GLASS WOOL PLUG
(PARTICULATE FILTER)
5 - TENAX-GC CARTRIDGE
6 - PORAPAK R CARTRIDGE
7 - AMBERSORB XE-340
CARTRIDGE

Figure 26. "Breadboarded" version of the portable miniature sampling system with sorbent tubes in series.



1 - BROOKS 500 cc/min ROTAMETERS
2 - RUBBER TUBING
3 - TENAX-GC SORBENT TUBE
4 - PORAPAK R SORBENT TUBE
5 - AMBERSORB XE-340 SORBENT TUBE
6 - ALTERNATE POSITIONS FOR TUBING
7 - NEEDLE VALVES
8 - SWAGELOK TEES
9 - PUMP PRE-FILTER
10 - DUPONT P4000 PUMP
11 - BUBBLE METER
12 - EXHAUST BARB

Figure 27. Schematic of the "breadboarded" version of the sampling system with the sorbent tubes in parallel.

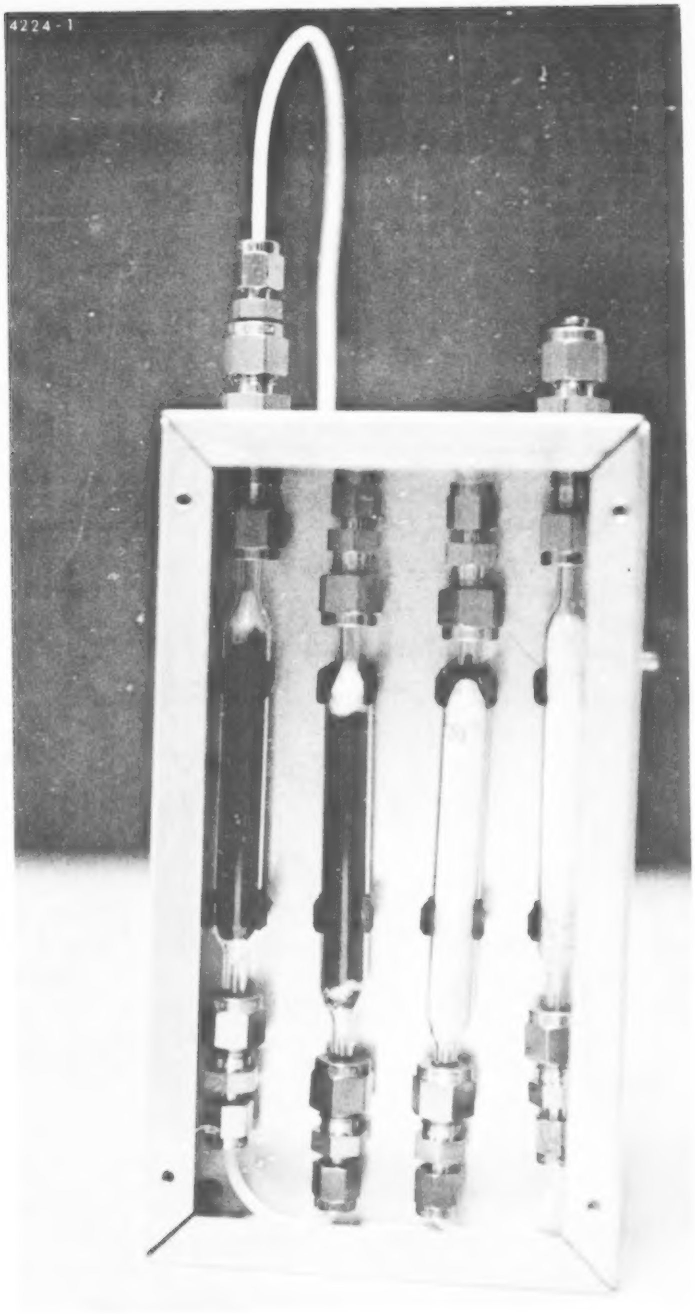


Figure 28. The "tube tray" portion of the Ambient Air Collection System.

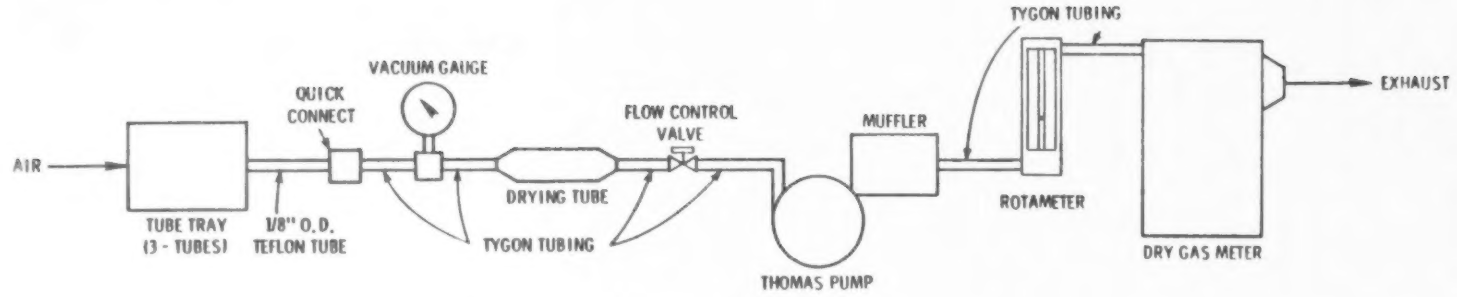
was not included with this sampler). This system was to be capable of attaining flow rates up to 10-15 L/min across a substantial pressure drop [maximum of 6.8×10^4 - 8.1×10^4 Pa (20-24 in. Hg)]. Laboratory evaluation of the Nutech Gas Sampler showed that flow rates of less than 3 L/min were attained with this sampler attached to a sorbent tube tray containing three sorbent tubes (Tenax-GC, Porapak R, and Ambersorb XE-340) in series. The Nutech system was then modified and connected to a large vacuum pump to evaluate the additional flow capabilities of the larger pump. Figure 29 gives schematics of the two systems evaluated and Figure 30 shows a plot of the results obtained. As indicated in Figure 30, the large vacuum pump increased the flow rate obtainable only slightly because pressure drop across the tube tray increased dramatically as flow rates increased. The specifications of the Nutech system superimposed on this plot demonstrate that it was performing properly. Therefore, the Nutech Gas Sampler, with its supplied pump, was adapted for use in the Ambient Air Collection System. More details on this sampler and its use in the Ambient Air Collection System are supplied in Appendix C of this report.

RESULTS

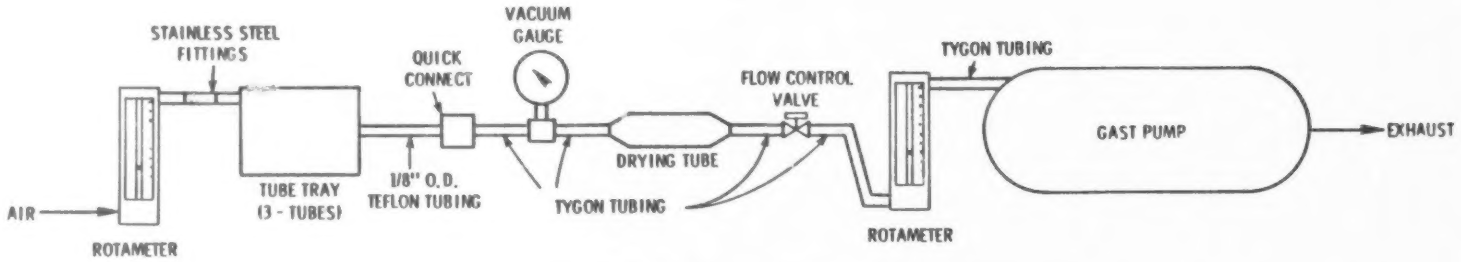
Based on laboratory evaluation, a multi-residue sampling system was developed for the collection of ambient air samples. This system, designed to collect a broad variety of organic compounds from the atmosphere, should effectively collect and subsequently release the compounds of interest for this project. An Operation Manual, given in Appendix C, was written in draft form prior to field evaluation of this sampling system and finalized for this report. This manual describes the preparation, fabrication, operation, and maintenance of the Ambient Air Collection System.

DISCUSSION

The Ambient Air Collection System combines, in series, three commercially available solid sorbent materials, each within a discrete glass cartridge. These sorbents, Tenax-GC, Porapak R, and Ambersorb XE-340, have complimentary adsorption characteristics. When combined in series in an air sampling system, each sorbent retains a certain range of compounds for subsequent analysis. Figure 31 displays the theoretical performance of a multi-residue sampling system. An ambient air sample contains a wide variety of compounds including those of high, intermediate, and low volatility (represented by squares, triangles, and circles, respectively, in Figure 31). All of the compounds in the air sample are concentrated to varying degrees on the first sorbent tube (Tenax-GC). Low volatility compounds (squares) are concentrated quantitatively at the head of the first tube. Such compounds experienced very little chromatographic displacement down the sorbent tube because they partition more into the stationary (sorbent) than mobile (air) phase of the system. Very


AIR
TUBE TRAY
(3 - TUBES)
1/8" O.D.
TEFLON TUBE
QUICK
CONNECT
VACUUM GAUGE
DRYING TUBE
TYGON TUBING
FLOW CONTROL
VALVE
THOMAS PUMP
MUFFLER
TYGON TUBING
ROTAMETER
DRY GAS METER
EXHAUST

A. SCHEMATIC OF NuTECH GAS SAMPLING SYSTEM


AIR
ROTAMETER
STAINLESS STEEL
FITTINGS
TUBE TRAY
(3 - TUBES)
1/8" O.D.
TEFLON TUBING
QUICK
CONNECT
VACUUM
GAUGE
DRYING TUBE
TYGON TUBING
FLOW CONTROL
VALVE
ROTAMETER
TYGON TUBING
GAST PUMP
EXHAUST

B. SCHEMATIC OF MODIFIED NuTECH STSYEM WITH GAST PUMP

Figure 29. Schematics of two sampling systems.

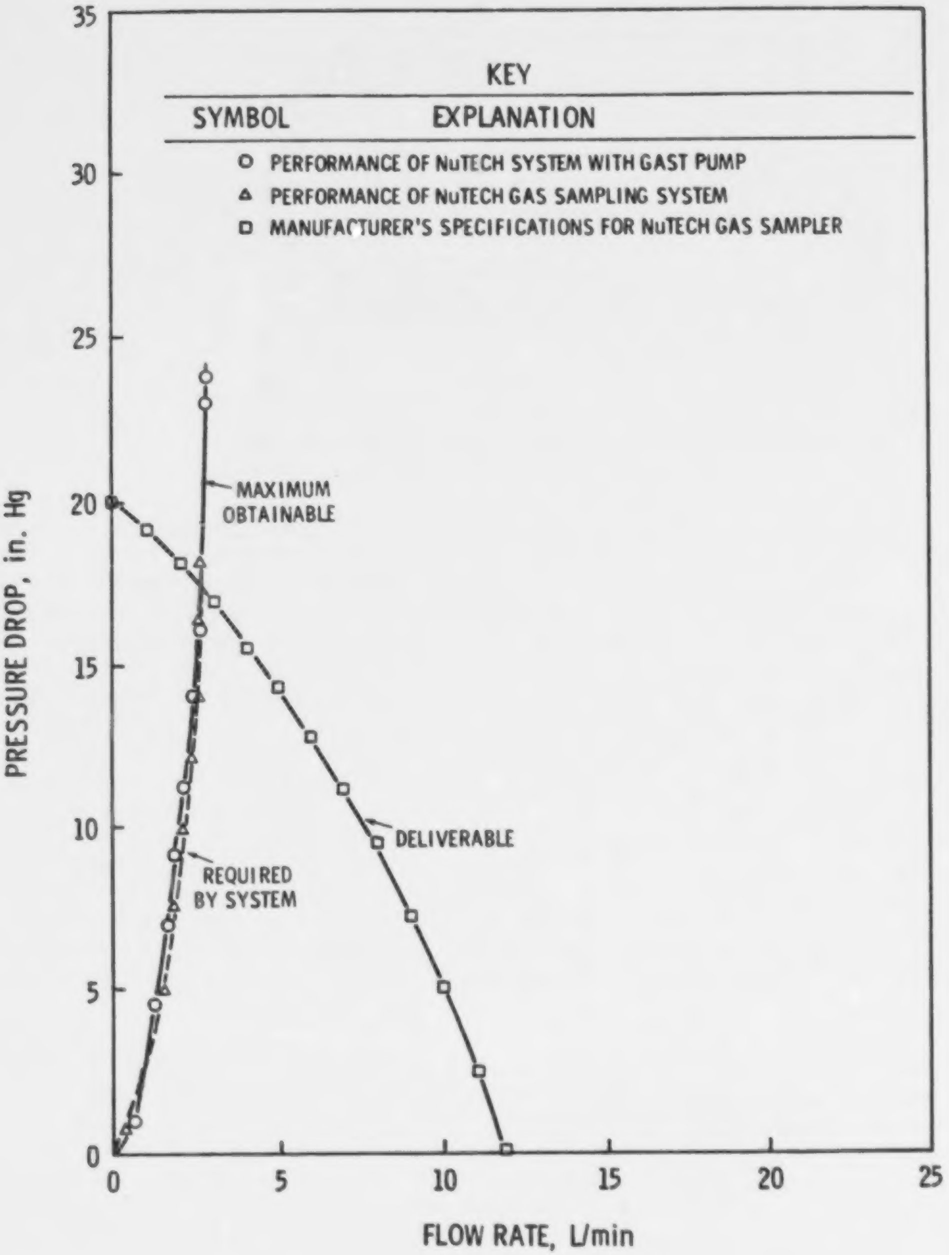


Figure 30. Plot of flow rate versus pressure drop performance of two sampling systems attached to a sorbent tube tray and manufacturer's specifications for the Nutech Gas Sampler.

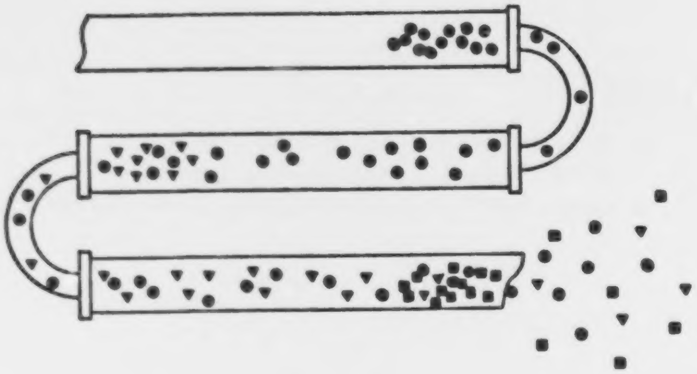


Figure 31. Theoretical performance of multi-residue sampling system.

volatile compounds (circles), however, partition mostly into the mobile (air) phase and rapidly pass through the first tube. They frequently are not concentrated to analytically detectable levels. Compounds of intermediate volatility (triangles) may be concentrated to detectable levels, but also eventually pass through the first sorbent tube. Intermediate and high volatility compounds which elute from the first tube pass into a second sorbent tube (Porapak R) which has greater affinity for volatile organics. Again, all compounds are concentrated on the second tube to varying degrees. Compounds partitioning more into the stationary (sorbent) than mobile (air) phase are retained while very volatile compounds are concentrated but eventually pass through this second tube as well. The very volatile compounds which pass into the third sorbent tube (Ambersorb XE-340) are retained by this tube. The ability of the Ambient Air Collection System to perform as theoretically described was evaluated with field samples. The results of these field evaluations are given in Sections 10 and 11.

In addition to the ability to collect atmospheric organics, the sorbent cartridges should also be able to release organics for analysis. As indicated previously, not all organics may be quantitatively released from the cartridges of the Ambient Air Collection System. In particular, very volatile, polar organics may be difficult to recover from the Ambersorb tubes. Consequently, field evaluations included a study of spiking techniques (see Sections 9 and 10).

SECTION 9

COLLECTION OF FIELD SAMPLES

OBJECTIVE

The purpose of the field sampling phase of this program was to test the newly developed sampling and analytical methodology under actual field conditions. This included evaluation of the difficulty of transporting the sampling system and accessories, of operating this system in the field, and, later, of analyzing complex environmental samples. The analyses of these samples are discussed in Sections 10 and 11.

INSTRUMENTATION

The Ambient Air Collection System which was developed for this project (see Section 8), was used to collect field samples. The Operation Manual for this system, given in Appendix C, describes the preparatory and sampling procedures for using this system, as well as the details of its fabrication. Although the operation manual was drafted prior to field sampling, experience gained during this work was used to modify the procedures in the original draft. These modifications are included in the final version of the manual presented in this report. Most of the modifications were relatively minor, such as wrapping sorbent tubes with glass wool to minimize breakage of sorbent and culture tubes. One exception was the mechanical leak check procedure (included in Appendix C), which was developed as the result of field sampling experience. This procedure was first instituted during the collection of samples in Houston, Texas.

FIELD SAMPLING

Dayton

Samples were collected at Carillon Park in Dayton, Ohio, under EPA Contract 68-02-2774. They were obtained with the use of the Portable Miniature Collection System developed for that contract. The results of these analyses are not given in this report; however, the results did cause a small modification to be made in the analytical system [$(GC)^2$/MS]. This modification is described in Section 10.

Los Angeles

The sampling plan developed for the collection of samples in Los Angeles is given in Table 26. In addition to those samples shown, samples were also collected with two Portable Miniature Collection Systems during the same time periods. Although total sample volumes collected by the Portable and Ambient Air Systems were different, the samples could be considered replicates. Extra, blank sorbent tubes were also taken on that sampling trip to replace any sorbent tubes broken during shipment. Spiking solutions are described in Tables 27 through 31.

Sampling personnel and all equipment were flown from Dayton to Los Angeles, with the equipment sent as baggage. The equipment was carefully packed in sturdy containers with plenty of cushioning packing material. Sorbent tubes were wrapped with glass wool inside the culture tubes to minimize breakage. No problems were encountered in shipment other than to assure airline officials that the materials inside were not hazardous and were securely packaged. No damage to equipment occurred on either the out-going or return flights, except the breakage of a few culture tubes.

The sampling site was on the roof top of the Education Resource Center Building located on the grounds of the California State University, Dominguez Hills campus. A map of the Los Angeles area, provided in Figure 32, shows the campus slightly north of area A. Areas A, B, and C correspond to locations estimated to be high in concentrations of the compounds of interest by computer Climatological Dispersion Modeling. Data for this model were obtained from the MRC Source Assessment Data Base which incorporates stack emission data from numerous sources. Table 32 gives the computer estimated composition of air pollution in these areas for some of the compounds of interest and a few others.

The samples were collected on 14 and 15 April 1980. On 14 April 1980 the temperature in Los Angeles ranged from approximately 18°C to 27°C (65°F to 80°F), the relative humidity from about 25% to 49%, and the winds from the northwest to west-southwest. On the following day, 15 April 1980, weather conditions were similar: the temperature range was approximately the same; the relative humidity slightly less and more stable (around 32%); and the winds more gusty, mainly from the northwest. Several exhaust stacks could be seen from the sampling location to the north, northwest, and southwest of the Dominguez Hills campus.

TABLE 26. SAMPLING PLAN - LOS ANGELES

Sample number	Sorbent	Purpose	Tray position	Sampling				Pump information	Other information
				Date	Times	Volume	Flow rate		
1	Tenax	Sample	1	4-14-80	~0800 -1600 hr	~1,000 L	~2-3 L/min	Ambient Air System, AC power, maximum flow	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
C	Tenax	Calibration	1	4-14-80 and 4-15-80					Calibration of sampling system flow rates.
	Porapak R	Calibration	2						
	Ambersorb	Calibration	3						
2	Tenax	Sample	1	4-15-80	~0800 -1600 hr	~1,000 L	~2-3 L/min	Ambient Air System, AC power, maximum flow	Field spike - see Method A
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
B	Tenax	Blank							Blanks
	Porapak R	Blank							
	Ambersorb	Blank							
FS	Tenax	Spike							Transport spikes - see Method B
	Porapak R	Spike							
	Ambersorb	Spike							
LS	Tenax	Spike							Lab spikes - see Method B
	Porapak R	Spike							
	Ambersorb	Spike							

Spiking Method A - ~5 min after starting sample collection, inject 1 μL quantities each of spiking solutions A, C, and E (see Tables 27, 29, and 30) into the glass wool plug of the system inlet.

Spiking Method B - Inject 1 μL quantities of each spiking solution ~3 mm (1/8 in.) into the sorbent beds of the tubes below at their unnumbered ends.

Tenax - C, E, F (See Tables 27 to 30)
Porapak R - A, B, C
Ambersorb - A

TABLE 27. FIELD SPIKING SOLUTION A

Compound	Concentration, µg/mL
Acrolein	93
Carbon tetrachloride	120
Vinyl acetate	132
Benzene	76
Acrylonitrile	81
Ethylene dichloride	56
1,4-Dioxane	133
Tetrachloroethylene	59
Ethylene dibromide	202
Acetone[a]	

[a] Solvent.

TABLE 28. FIELD SPIKING SOLUTION B

Compound	Concentration, µg/mL
Tetrachloroethylene	55
cis-1,3-Dichloropropane	77
trans-1,3-Dichloropropene	76
Hexachloro-1,3-butadiene	163
Acetone[a]	

[a] Solvent.

TABLE 29. FIELD SPIKING SOLUTION C

Compound	Concentration, µg/mL
Styrene	92
Hexachloro-1,3-butadiene	191
Benzyl chloride	98
Acetone[a]	

[a] Solvent.

TABLE 30. FIELD SPIKING SOLUTION E

Compound	Concentration, μg/mL
Ethylene glycol	151
Di-(2-ethylhexyl) phthalate	42
Pentachlorophenol	68
Acetone[a]	

[a] Solvent.

TABLE 31. FIELD SPIKING SOLUTION F

Compound	Concentration, μg/mL
Benzidine	73
Chrysene	24
Benzo(a)pyrene	47
Toluene[a]	

[a] Solvent.

TABLE 32. LOS ANGELES - POTENTIAL CARCINOGENIC COMPOSITION AT POINTS OF MAXIMUM CONCENTRATION (micrograms per cubic meter)

Compound	Location A 86, 46	Location B 80, 46	Location C 82, 46
Acrylonitrile	0.0007	0.0030	0.0016
Benzene	0.01	0.01	0.01
Carbon tetrachloride	44	5	9
Chloroform	22	2	4
DDT	0.38	24.7	1.4
Ethyl Chloride	6	5	6
Ethylene dichloride	191	22	42
Vinyl chloride	117	12	23
Vinylidene chloride	0.16	0.05	0.02

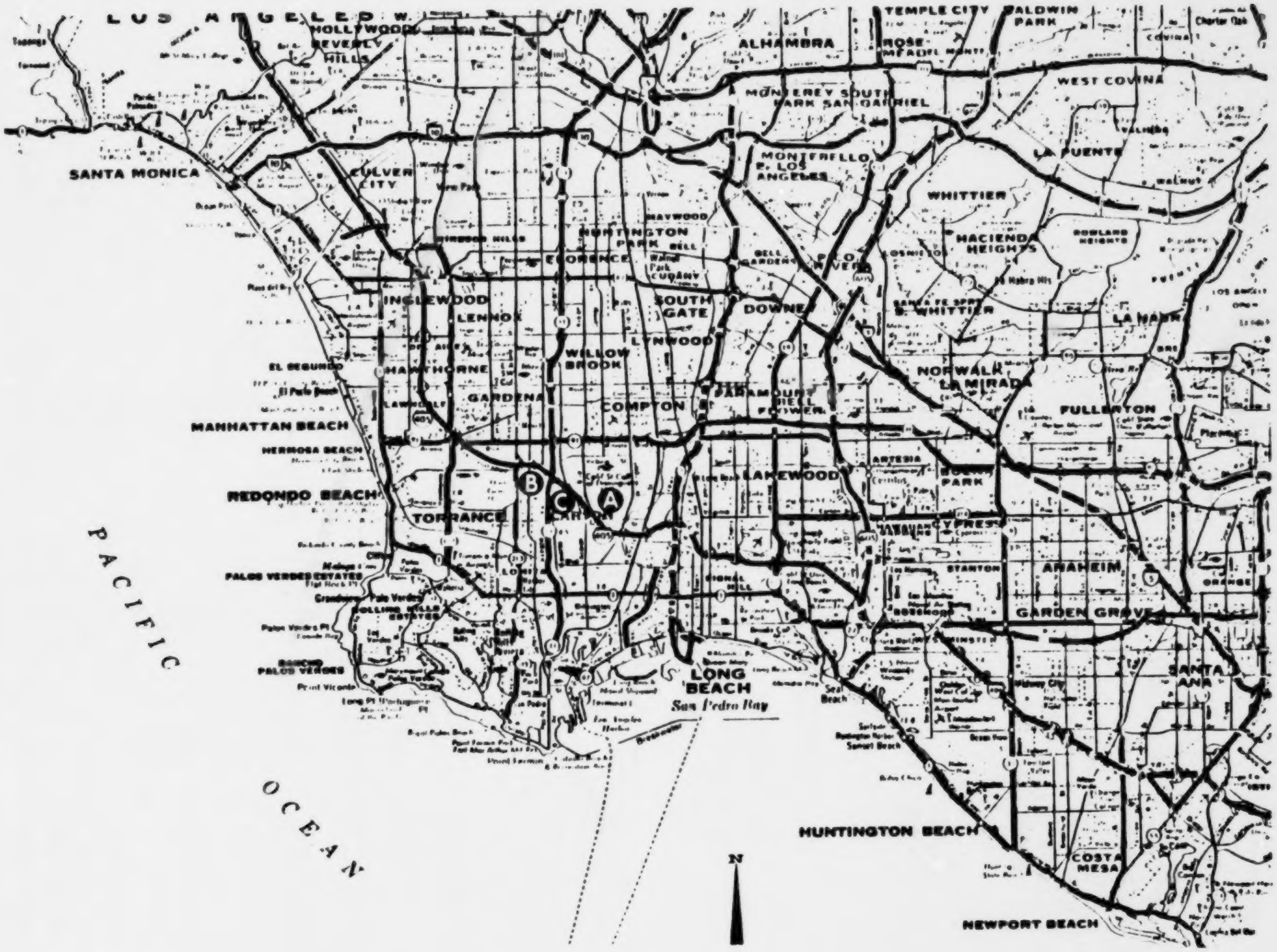

LOS ANGELES
HOLLYWOOD
BEVERLY HILLS
SANTA MONICA
CULVER CITY
ALHAMBRA
ROSEMEAD
TEMPLE CITY
BALDWIN PARK
WEST COVINA
MONTEREY PARK
SOUTH SAN GABRIEL
MONTEBELLO
E. LOS ANGELES
LA PUENTE
WHITTIER
HACIENDA HEIGHTS
ROWLAND HEIGHTS
HUNTINGTON PARK
MAYWOOD
BELL
FLORENCE
SOUTH GATE
DOWNEY
PICO RIVERA
BELL GARDENS
CUDAHY
S. WHITTIER
LA HABRA
INGLEWOOD
LENNOX
LYNWOOD
WILLOWBROOK
HAWTHORNE
EL SEGUNDO
GARDENA
COMPTON
PARAMOUNT
BELLFLOWER
NORWALK
LA MIRADA
FULLERTON
MANHATTAN BEACH
HERMOSA BEACH
REDONDO BEACH
TORRANCE
CARSON
A
B
C
LAKEWOOD
ARTESIA
BUENA PARK
CYPRESS
STANTON
ANAHEIM
ORANGE
GARDEN GROVE
SANTA ANA
PALOS VERDES ESTATES
ROLLING HILLS
RANCHO PALOS VERDES
LONG BEACH
SIGNAL HILL
San Pedro Bay
Seal Beach
HUNTINGTON BEACH
COSTA MESA
NEWPORT BEACH
PACIFIC OCEAN
N

Figure 32. Locations of high ground level concentrations - Los Angeles, California.

Table 33 describes the sampling conditions. No problems were experienced with the Ambient Air Collection System.

Niagara Falls

The ability of the Ambient Air Collection System to sample unattended was tested during an indoor sampling trip in Niagara Falls. The sampling plan is given in Table 34. As indicated, three, consecutive, twelve-hour samples were to be taken with the system unattended during the majority of the sampling periods. Samples were collected in a private residence with temperatures ranging from 24°C to 27°C (75° to 81°F). As indicated in Table 35, this system did not function well under these strenuous circumstances with discontinuous operation during the second and third sampling periods. Maitenance performed on the system's pump, after returning to the laboratory, corrected the malfunction.

Houston

The sampling plan developed for the collection of Houston air samples is given in Table 36. In addition to those samples shown, samples were also collected with three Portable Miniature Collection Systems and a critical orifice system developed for another project. Although total sample volumes collected by these three different systems were not identical, the samples were essentially replicates. Extra, blank sorbent tubes were taken to replace broken tubes and tubes spiked with the Sample Generation System were taken to provide transport and field spikes.

As with Los Angeles, personnel and equipment were flown to Houston. This time, airline officials were especially concerned that the materials and/or equipment might be hazardous. They were assured there was absolutely no hazard. Although the sorbent tubes were wrapped with glass wool inside the culture tubes, at least a dozen culture tubes broke during shipment. This damage was attributed to the soft-sided case in which they were packed. A sturdy case lined with cushioning materials would have been preferable.

The sampling was performed on the second floor balcony of a motel located 0.4 Km (1/4 mile) north of Route 225 on South Richie Road. This site was within area number 3 on the map shown in Figure 33. As with Figure 32, the locations marked on this map are areas estimated to have high levels of the pollutants of interest. This information was obtained by computer Climatological Dispersion Modeling with data from the MRC Source Assessment Data Base [1]. The estimated composition of some of the selected compounds and a few others in these areas are given in Table 37. The terrain surrounding the sampling area selected was relatively flat and oil refineries could be seen approximately 1.6 Km (1 mile) away in all directions.

TABLE 33. SAMPLING CONDITIONS - LOS ANGELES

Sample number	Date	Times	Dry gas meter volume, L	Flow rate, L/min	Volume estimated from flow rate, L	Comments
1	4-14-80	1007-1807 hr	1711.3	∿3.7	∿1,780	Backup Ambersorb tube chipped upon removal. No pump problems.
2	4-15-80	0810-1610 hr	974.5	∿2.0	∿960	No pump problems. Spiked as directed.

TABLE 34. SAMPLING PLAN - NIAGARA FALLS

Sample number	Sorbent	Purpose	Tray position	Sampling Date	Sampling Times	Sampling Volume	Sampling Flow rate	Pump information	Other information
1	Tenax	Sample	1	6-18-80	∿0800-2000 hr	∿1,400 L	∿2 L/min	Ambient Air System, AC power, maximum flow.	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
2	Tenax	Sample	1	6-18-80 to 6-19-80	∿2100-0900 hr	∿1,400 L	∿2 L/min	Ambient Air System, AC power, maximum flow.	
	Porapak	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
3	Tenax	Sample	1	6-19-80	∿1000-2200 hr	∿1,400 L	∿2 L/min	Ambient Air, System, AC power, maximum flow	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
B	Tenax	Blank							Blanks.
	Porapak R	Blank							
	Ambersorb	Blank							
C	Tenax	Calibration		6-18-80 and 6-19-80				-	Calibration of sampling system flow rates.
	Porapak R	Calibration							
	Ambersorb	Calibration							
	Ambersorb	Calibration							

TABLE 35. SAMPLING CONDITIONS - NIAGARA FALLS

Sample number	Date	Times	Dry gas meter volume, L	Flow rate, L/min	Volume estimated from flow rate, L	Comments
1	6-18-80	0809-2010 hr	1430	∿2	∿1,400	No problems.
2	6-18-80 to 6-19-80	2112-? hr	680	∿2	?	Pump stopped during sampling period.
3	6-19-80	1012-2202 hr	720	∿2	?	Pump stopped during sampling, started again by tapping.

TABLE 36. SAMPLING PLAN - HOUSTON

Sample number	Sorbent	Purpose	Tray position	Sampling				Pump information	Other information
				Date	Times	Volume	Flow rate		
1	Tenax	Sample	1	7-29-80	0800-1600 hr	∿1,000 L	∿2 L/min	Ambient Air System, AC power flow ≤2 L/min.	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
2	Tenax	Sample	1	7-30-80	0800-1600 hr	∿1,000 L	∿2 L/min	Ambient Air System, AC power flow ≤2 L/min	
	Porapak R	Sample	2						
	Ambersorb	Sample	3						
	Ambersorb	Backup	4						
B	Tenax	Blank							Blanks.
	Tenax	Blank							
	Porapak R	Blank							
	Porapak R	Blank							
	Ambersorb	Blank							
	Ambersorb	Blank							
S	Tenax	Spike							Spikes - spiked with ∿5 μg each of benzene, benzyl chloride, carbon tetrachloride, tetrachloroethylene, ethylene dibromide, cis-1,3-dichloropropene, and hexachloro-1,3-butadiene on Sample Generation System (Appendix B).
	Tenax	Spike							
	Porapak R	Spike							
	Porapak R	Spike							
	Ambersorb	Spike							
	Ambersorb	Spike							
C	Tenax	Calibration	1	7-29-80 and 7-30-80					Calibration of sampling system flow rates.
	Porapak R	Calibration	2						
	Ambersorb	Calibration	3						
	Ambersorb	Calibration	4						

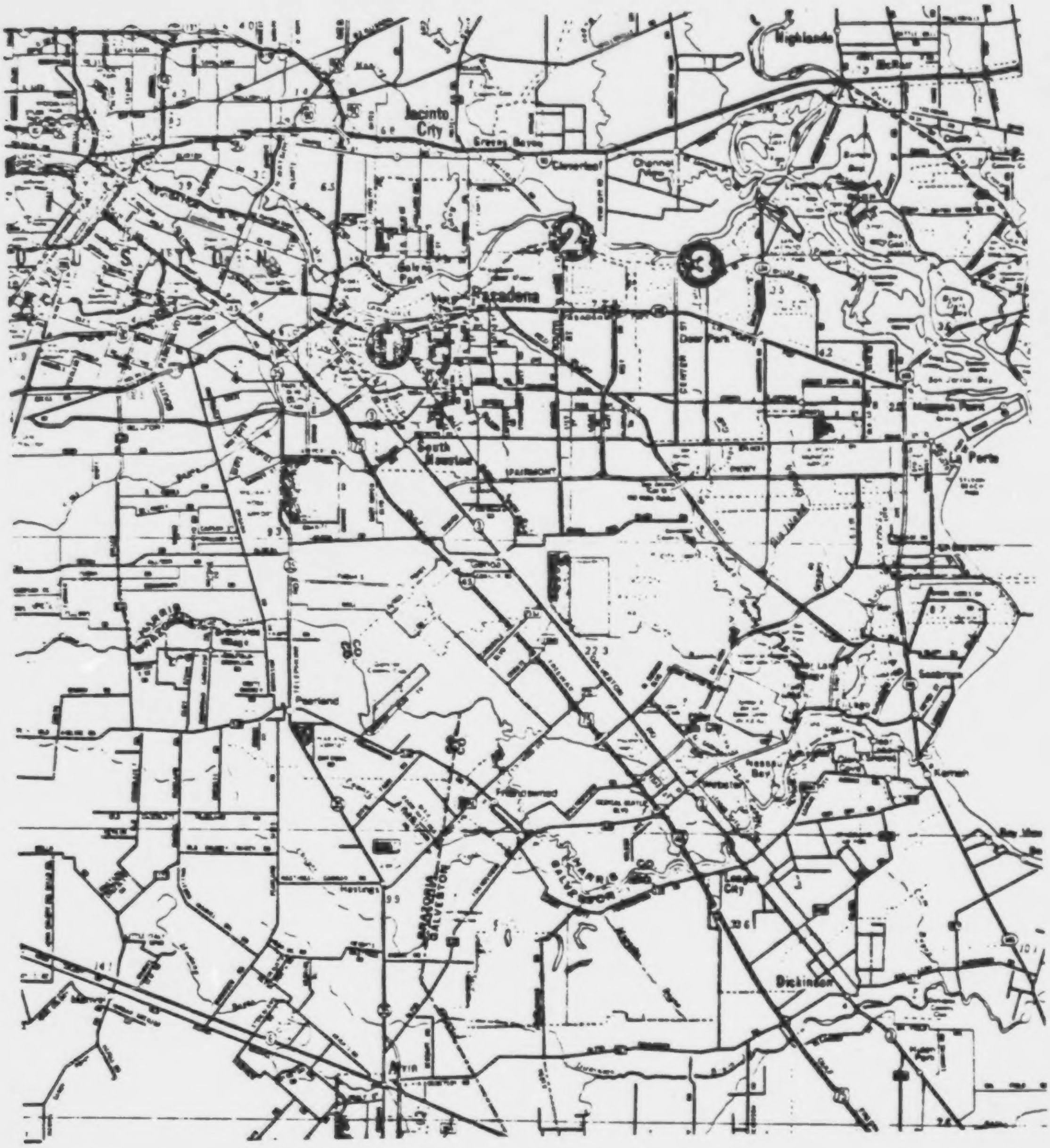

Highlands
Jacinto City
Channelview
2
3
Pasadena
1
South Houston
La Porte
Pearland
Friendswood
League City
Dickinson
Hastings
Alvin

Figure 33. Locations of maximum concentration of pollutants in Houston.

TABLE 37. AVERAGE CONCENTRATIONS AT POINTS OF MAXIMUM POLLUTION IN HOUSTON
[Micrograms per cubic meter]

Compound	Location 1 82,88	Location 2 90,92	Location 3 95,90
Acrylonitrile	1.0	0.1	0.1
Benzene	1,366.0	6.0	5.0
Carbon tetrachloride	6.0	190.0	251.0
Chloroform	2.0	92.0	123.0
Dichlorobutene	1.0	0.02	0.02
Ethylene dichloride	26.0	977.0	757.0
Tetrachloroethane	0.009	0.022	0.018
Epichlorohydrin	0.15	1.0	1.0
Trichloroethylene	5.0	12.0	10.0
Vinyl chloride	7.0	15.0	2.0
Vinylidene chloride	0.004	0.165	0.220
Ethylene dibromide	0.14	0.01	0.10

The samples were collected on 29 and 30 July 1980. Weather conditions were hot and humid both days, with temperatures exceeding 32°C (90°F) and relative humidity at approximately 90%. The sampling conditions are provided in Table 38. As mentioned previously, the leak check procedure specified in the Operation Manual (Appendix C) was instituted during this sampling program.

TABLE 38. SAMPLING CONDITIONS - HOUSTON

Sample number	Date	Times	Dry gas meter volume, L	Flow rate, L/min	Volume estimated from flow rate, L	Comments
1	7-29-80	1148-1948 hr	461	~1	~480	No problems.
2	7-30-80	0756-1556 hr	626	~1.5	~720	No problems.

SECTION 10

ANALYSIS OF FIELD SAMPLES BY CAPILLARY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

OBJECTIVE

Samples of ambient air which were collected in the field with the Ambient Air Collection System were to be analyzed by capillary gas chromatography/mass spectrometry [$(GC)^2$/MS]. The analytical method, described in Section 7, for $(GC)^2$ analyses was adapted to a $(GC)^2$/MS instrument for the evaluation of the field samples. The presence of the twenty selected potential carcinogens was investigated by reviewing mass spectral data. Compounds of interest identified in the field samples were then quantitated.

INSTRUMENTATION

A Hewlett-Packard Model 5985 GC/MS system was used for the analysis of field samples. This instrument had a Model 5840 GC with a capillary inlet system which was very similar to the GC used during the analytical method development phase of this program (Section 7). A data system, that was also part of this instrument, was used to display, interpret, and reduce mass spectral data. Final interpretation of mass spectral data was performed by a qualified mass spectroscopist.

To introduce samples from sorbent tubes into this analytical system, the capillary inlet system (Section 7) was interfaced to the Model 5985 GC/MS. Some modifications to the inlet system, GC/MS, and analytical method were necessary to obtain an interface which produced acceptable results. For the analysis of field samples from Houston, Texas, the capillary inlet system was removed from the GC/MS and installed on the multi-detector $(GC)^2$ instrument described in Section 11. A Nutech Model 320 Thermal Desorption System, a commercially available sample introduction system similar to the capillary inlet system, was then interfaced with the GC/MS. Houston field samples were analyzed with both the GC/MS and the multi-detector $(GC)^2$ instruments.

EVALUATION

The capillary inlet system devised during analytical method development was initially installed on the GC of the Model 5985

GC/MS with the inlet system/GC interface maintained in its exact physical and functional configuration. Preliminary evaluations demonstrated that this system was operating properly with this configuration. These evaluations were performed by analyzing column test mixtures which were previously used to specify analytical performance during analytical method development (discussed in Section 7). Analyses of these mixtures were performed in the split injection mode, the mode used during method development, with injections made through a septum tee into an empty glass tube installed in the inlet system (see Figure 15, Section 7). Although the results demonstrated proper performance of the inlet system, the mass spectrometer was not as sensitive as the flame ionization detector (FID) used during method development. All of these experiments were performed with the mass spectrometer operated under electron impact ionization in a continuously scanning mode.

To improve analytical sensitivity, the inlet system was evaluated with very-low split and splitless injection operation. During splitless operation some compounds in the test mixtures were found to be catalytically altered. These *in situ* reactions were detectable with mass spectral information, but would not be identifiable with an FID (as previously used). Splitless operation also decreased the flow of carrier gas removing sample from the capillary inlet system trap. This extended the period of time to effectively transfer the sample from this trap to the GC and resulted in broadened chromatographic peaks, especially for low-boiling constituents. The problems of peak-broadening and catalytic alteration were found to decrease as the injection mode was changed from splitless to low-split to moderate-split operation. By periodically changing the nickel capillary trap of the inlet system, by maintaining uniform heating of the trap during desorption, and by adjusting instrument operating parameters, the problems of peak-broadening and catalytic alteration with splitless injection were found to be significantly reduced.

As part of the preliminary evaluations of the $(GC)^2/MS$ analytical system, field samples were collected near the laboratory to provide authentic samples for analysis. As indicated in Section 7, these samples were collected at Carillon Park in Dayton, Ohio, under EPA Contract 68-02-2774. They were obtained with the use of the Portable Miniature Collection System developed for that contract and, therefore, the results of these analyses are not given in this report. However, the results impacted on this project by demonstrating the necessity of splitless injection operation in order to obtain suitable sensitivity for field samples.

Frequent adjustment, trap changing, and cleaning of the capillary inlet system were found to be necessary to maintain acceptable operation of the analytical system using this system and splitless operation. A commercial sample introduction system obtained previously was therefore interfaced to the Model 5985 GC/MS for the analysis of Houston field samples. This system was a Nutech Model 320 Thermal Desorption System. Concurrently, the capillary inlet system was interfaced to a multi-detector (GC)^2 system (Section 11). Both systems were comprised of the same major elements: thermal desorption chamber, heated valve, capillary trap, and thermal control unit. Sample reconcentration and introduction into the analytical systems were performed in the same manner; however, some of the physical details of these two systems varied. For example, the trap of the Nutech system was contained in such a manner that the thermal control unit controlled both the cooling and heating of this trap. This was an advantageous convenience. Both systems were found to perform satisfactorily.

Another change made prior to the analysis of the Houston field samples was to change the mode of sample introduction from splitless to direct injection. To accomplish this modification, the carrier flow directed to the sample introduction system (Nutech) was modified in the Model 5985 GC/MS system. Instead of being obtained from a split off of the capillary inlet pneumatics (see Figure 10, Section 7), the carrier gas was supplied from a separate auxiliary system with an independent pressure controller. Furthermore, instead of introducing a sample from the trap into the GC through a needle inserted in the GC injection port, a direct coupling was made between the Nutech system and the GC column. In the GC/MS this was done with glass-lined stainless steel tubing (passing through the GC injection port for heat) with low-dead-volume stainless steel connections to the Nutech system and capillary column. To accomodate potentially greater sample quantities, the capillary column within the GC/MS was changed from an $\sim$50 M long, 0.2 mm ID, OV-101 fused-silica WCOT column to an $\sim$60 M long, 0.25 mm ID, SE-30 glass WCOT column. (Both columns had non-polar, methyl-silicone liquid phases making them somewhat equivalent in chromatographic characteristics.) Carrier gas flow through the Nutech system directly passed into the capillary column. The flow rate of this carrier was controlled by the pressure controller of the auxiliary system. The multi-detector (GC)^2 system also was interfaced to the capillary inlet system to permit direct sample injection as described in Section 11.

RESULTS

As noted previously, analyses were conducted using a Hewlett-Packard 5985A GC/MS/Data System having a 50-meter fused silica column coated with methyl silicone liquid phase. This was later changed to a 60-meter glass capillary column having an equivalent phase. Chromatographic conditions were varied to meet the individual demands of specific samples. When possible, all sorbents from a single sampling run were analyzed using the same temperature program so that retention values could be compared. Samples collected in Los Angeles and Niagara Falls were analyzed using the original capillary trap and inlet system designed and constructed as a part of this program (Section 7). Samples collected in Houston were analyzed using a Nutech Corporation Model 320 Thermal Desorption System. The latter unit was connected directly to the capillary analytical column of the GC/MS system. The two units offer essentially the same features; however, the Nutech system is more convenient to operate. This research effort was conducted with a companion program for the development of a portable miniature collection system. Thus, in some instances, data from parallel sampling conducted under that program will be used to illustrate results pertinent to this project.

A basic premise of the multiple sorbent sampling approach is that, for ambient air sampling in the complex and often hostile environments frequently encountered, compounds of interest are often not completely retained by a single sorbent. This would be particularly true when the volume of air sampled is large. The results presented for the three locations sampled adequately demonstrate this fact.

Calibration for Compounds on the Twenty Potential Carcinogen List

Compounds on the list of twenty potential carcinogens being studied in this program, if found to be present, were quantitatively measured. Calibration was achieved by preparing sorbent tubes with known weights of each material using a standard gaseous Sample Generation System constructed at MRC. This system is based on controlled syringe injection, vaporization and subsequent serial dilution of the standard compounds (Appendix B). Quantification by GC/MS was achieved by integration of the peak corresponding to a major interference-free ion of the compound which appeared at the correct predetermined retention value.

Qualitative identification of other components was achieved by initially using a standard compilation of mass spectral data [8]. Several collections of complete mass spectra are available and were used for more detailed spectral analyses. In some cases, compounds have been identified by class and carbon number such as C_{10}-alkane or C_4-alkylbenzene. In the latter case, the total carbon number of the alkyl moieties is given. For the data obtained on the Houston samples, an attempt was made to identify the specific compound where possible. Due to the similarity in fragmentation pattern of hydrocarbons under electron-impact, and because of the lack of strong molecular ions for highly branched hydrocarbons, boiling point data were used to select the one compound from several which might fit a mass spectrum.

Los Angeles Air Sampling Analysis

The atmospheric conditions and the sampling location in metropolitan Los Angeles are given in Section 9 of this report.

Figure 34 presents the chromatograms (total ion current plots) of materials retained on each of the sorbents from a single sampling run. The chromatogram at the bottom of the figure shows compounds retained in the Tenax-filled collector, while chromatograms for materials from the Porapak R and Ambersorb XE-340 collectors are shown in the middle and upper parts of the figure. At the top of the figure, a chromatogram of the contents of the backup Ambersorb XE-340 collector is shown.

These data are for samples collected with the portable miniature system; however, replicate samples showing the same features were collected using the Ambient Air Collection System.

By comparing the compounds retained by each of the sorbents, it is apparent that many compounds of interest escape collection on the Tenax and are retained in the Porapak and Ambersorb collectors. Benzene, for example, appears largely in the latter two collectors. Tetrachloroethylene, while appearing in the Tenax collector, is heavily concentrated in the Porapak R collector. Both of these compounds are included among the twenty potential carcinogens selected for evaluation in this program. Another compound of some interest is trichloroethane. This compound is found to reside essentially in the Ambersorb and Porapak R collectors.

Sampling system break-through is found to be minimal as shown by analysis of the Ambersorb backup collector which is the fourth tube in the collection series. The single, large peak observed from this collector is due to carbon dioxide.

The chromatograms in Figure 34 are normalized on the intensity of the strongest peak in each chromatogram. For quantitative comparison of one chromatogram to any of the others shown in that figure, absolute intensities must, of course, be compared. Accordingly, absolute peak area counts were used as the basis for the foregoing observations. Table 39 presents the amount of benzene and tetrachloroethylene found in each sorbent tube and the concentration of these compounds in the sampled air.

TABLE 39. SUBJECT COMPOUNDS PRESENT IN SAMPLES COLLECTED IN METROPOLITAN LOS ANGELES

Compound	Weight per collector, ng			Total weight, ng	Concentration,[a] ng/m^3 in air
	Tenax-GC	Porapak R	Ambersorb		
Benzene	87	111	8	206	120
Tetrachloroethylene	99	62	-	161	94

[a] 1711.3 liters of air sampled.

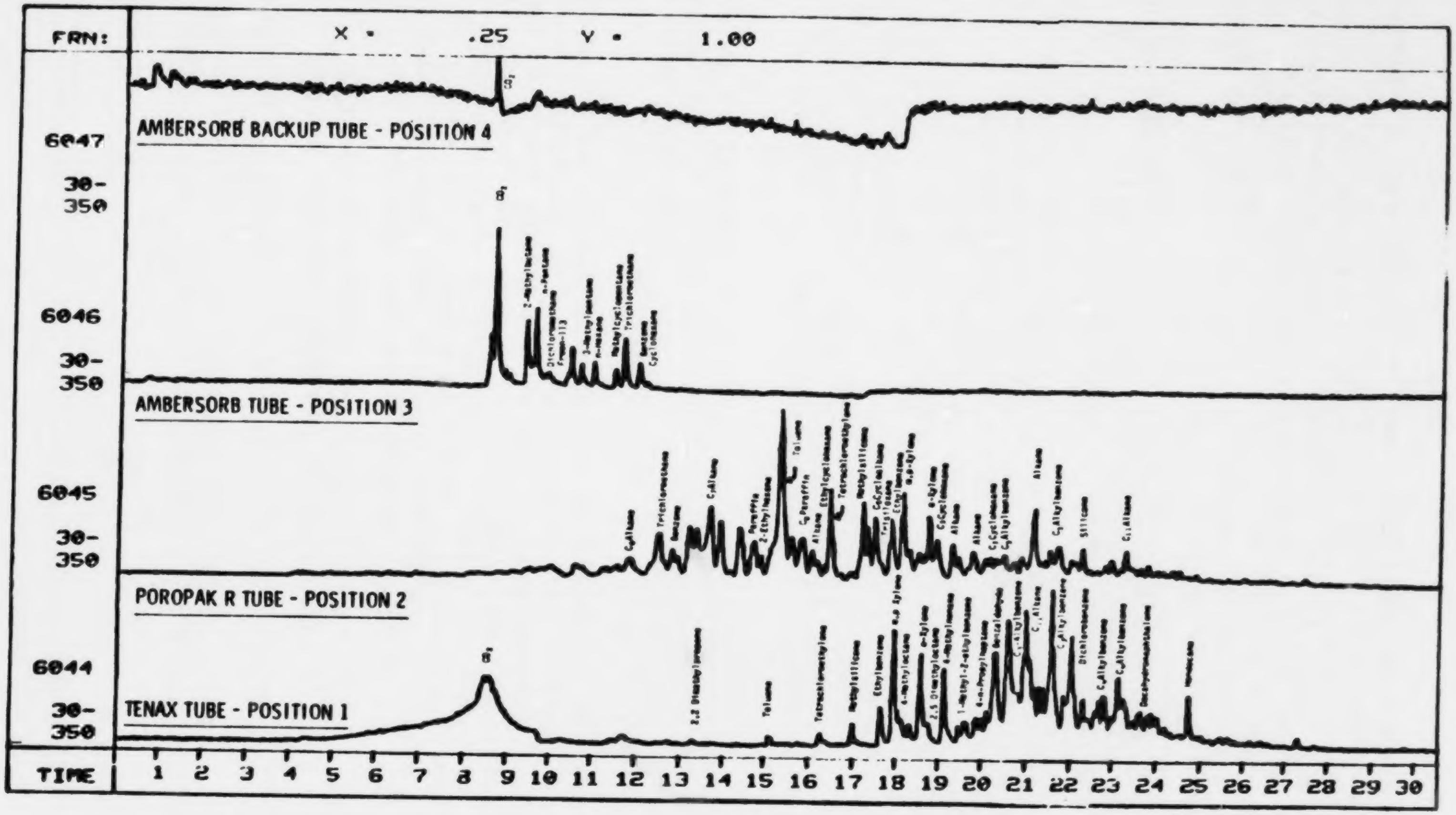


Figure 34. Reconstructed total ion chromatogram of materials collected in metropolitan Los Angeles by the multisorbent air sampling technique.

Niagara Falls Air Sampling Analysis

Sampling conducted in Niagara Falls, New York was of particular interest to this program because it provided a rather sheltered sampling environment. Sampling was conducted indoors where atmospheric oxidants (ozone, NO_x) were presumably at a low level, temperature and humidity were moderate, and the contribution to the sample matrix by various common mobile and stationary emission sources was minimal. The unattended performance of the sampling systems was tested and a discussion of this aspect of the operation is presented in Section 9.

Though the purpose of the sampling was to quantitate three specific compounds, benzene, tetrachloroethylene and trichloroethylene, all twenty potential carcinogens were included in the data evaluation. A total ion chromatogram of the contents of a Tenax collector is presented in Figure 35. A list of detected compounds is keyed by peak number to this chromatogram and is given in Table 40. As is shown by the chromatogram, the sample size significantly exceeded the capacity of the column, resulting in broadened chromatographic peaks. An important finding, however, was that even with the high sample loading and the large volume of air sampled, no sample breakthrough to the other sorbents in the series occurred. Total ion chromatogram from analyses of the Porapak R and Ambersorb tubes are shown in Figure 36. The data system software, as mentioned previously, normalizes the most intense peak to full-scale. In these cases, trace components or base-line perturbation due to water were normalized to full-scale. Mass spectra, however, show that the only components present are several silicone compounds, which are probably artifacts of the analytical system.

Quantitation of four compounds among the twenty subject carcinogens was conducted and is presented in Table 41.

Houston Air Sample Analysis

The results from the Niagara Falls, New York sampling indicated that sample breakthrough, and the resultant need for the multisorbent sampling system, may depend upon sample matrix and/or sampling conditions. To further evaluate this possibility, a field sampling trip was scheduled to take place in Houston, Texas during a sustained period of record high temperatures, accompanied by high humidity. During the time of actual sampling, the temperature ranged in the nineties and relative humidity was $\sim$90%.

Several modifications in the analytical system were made prior to analysis of the collected samples. Since a heavy loading of compounds was expected in these samples, the narrow-bore, fused-silica GC capillary column was replaced with a similar larger-bore glass column of about the same length. A methyl silicone liquid phase was retained. The capillary trapping and inlet

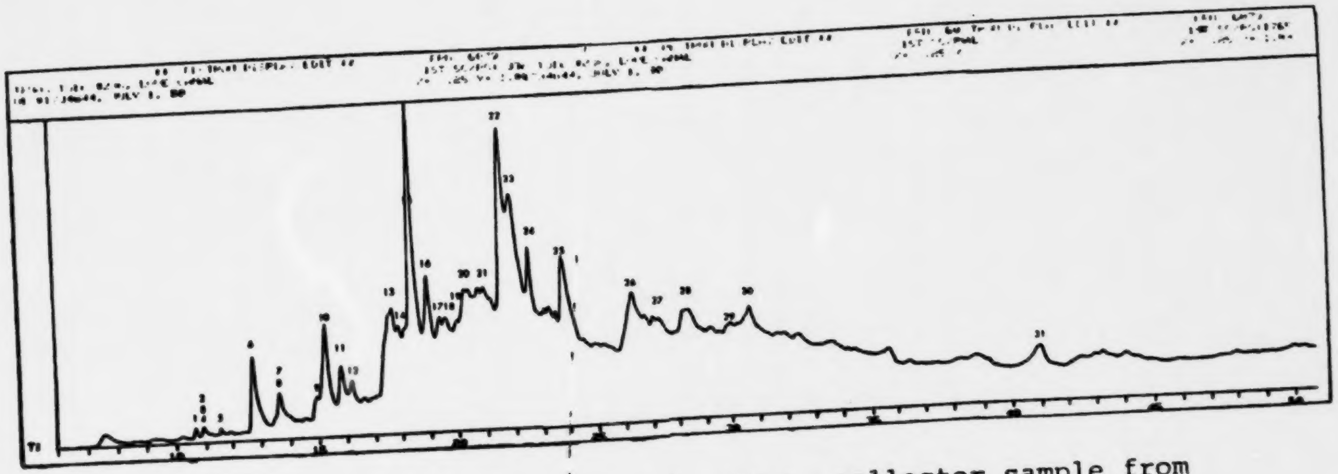


Figure 35. Qualitative scan of a Tenax collector sample from Niagara Falls sampling with the Ambient Air System.

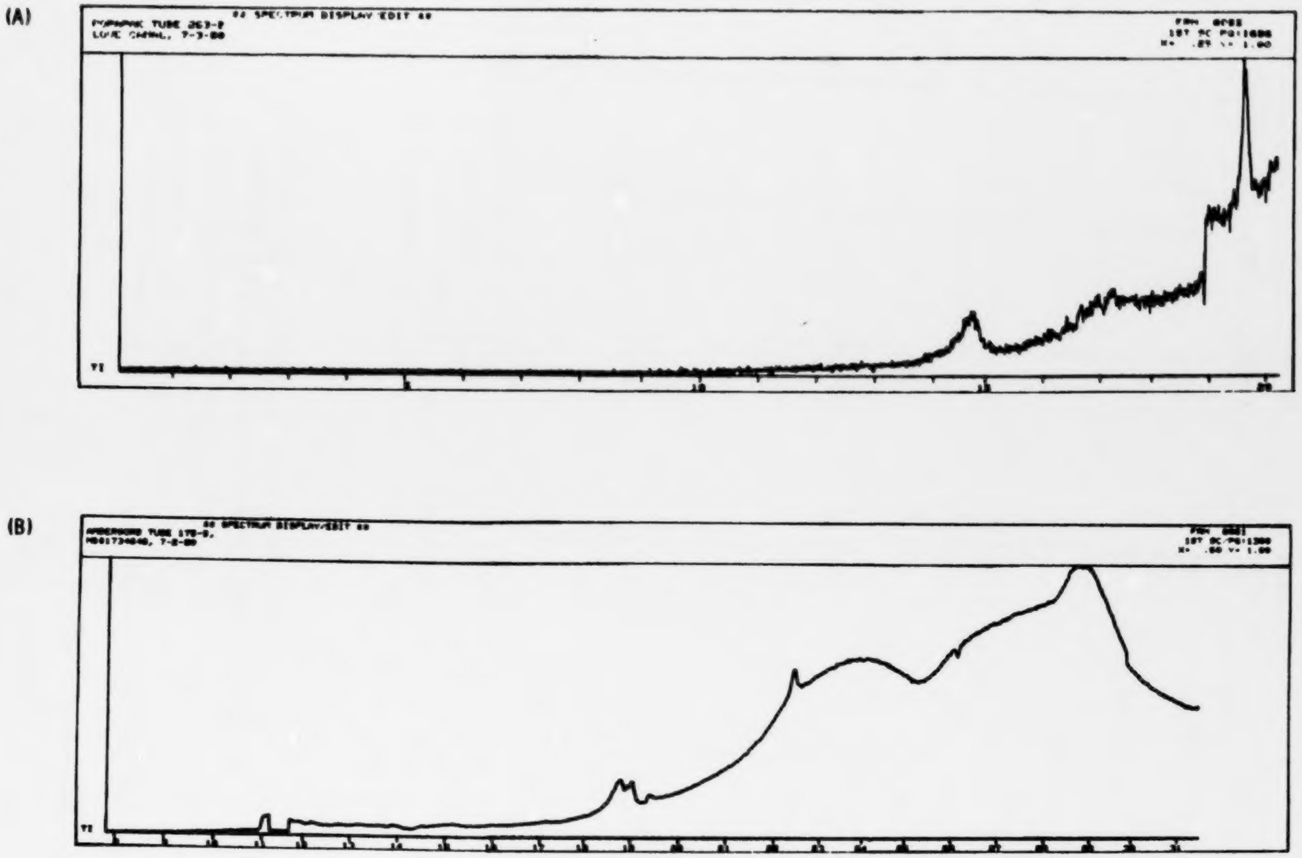


Figure 36. Reconstructed total ion chromatograms from GC/MS analysis of second and third collectors from Niagara Falls Sampling, A) Porapak R; B) Ambersorb XE-340.

TABLE 40. COMPOUNDS DETECTED IN AMBIENT AIR SAMPLES COLLECTED INDOORS AT NIAGARA FALLS

	Compound[a]	Chromatographic retention time, min	Ambient[b] Air Sampler	Ambient[b] Air Sampler	Portable Sampler
1.	1,1,1-Trichloroethane	10.6	X	X	X
2.	Benzene	10.9	X	X	X
3.	Cyclohexane	10.9	X	X	X
4.	Carbon tetrachloride	10.9	X	X	X
5.	C_7-Alkane	11.6	X	X	X
6.	Toluene	12.8	X	X	X
7.	Perchloroethylene	13.6	X	X	X
8.	C_8-Alkane	13.6	X	X	X
9.	Ethylbenzene	15.0		X	X
10.	Xylene	15.3	X	X	X
11.	Xylene	15.8	X	X	X
12.	C_9-Alkane	16.2	X	X	X
13.	o-Chlorotoluene	17.6	X	X	X
14.	Acetophenone	18.1		X	X
15.	Silicone[c]	18.5	X	X	X
16.	Dichlorobenzene, m/p	19.0	X	X	X
17.	C_4-Alkylbenzene	19.4	X	X	X
18.	o-Dichlorobenzene	19.5	X		X
19.	C_4-Alkylbenzene	20.0		X	X
20.	Silicone	20.3	X		X
21.	C_4-Alkylbenzene	20.8	X	X	X
22.	Silicone	21.7			X
23.	Dichlorotoluene	22.0	X	X	X
24.	Silicone	22.6			X
25.	Silicone	23.9			X
26.	Trichlorotoluene	26.4	X	X	X
27.	Silicone	27.1			X
28.	Tetrachlorobenzene	28.2	X	X	X
29.	Alkane	29.9			X
30.	2,3-di-t-Butyl-4-methylphenol	30.7			X
31.	Silicone	40.9			X

[a] Compound number is used to key chromatogram shown in Figure 35.

[b] These samples also show chlorobenzene and trichloroethylene.

[c] Silicone components arise from system silanization and septum bleed.

TABLE 41. SUBJECT COMPOUNDS DETECTED IN SAMPLES COLLECTED INDOORS AT NIAGARA FALLS

Compound	Mass,[a] ng	Volume air sampled, liters	Concentration, ng/m³
Benzene	1,970	1136.9	1,730
Tetrachloroethylene	8,770	1136.9	7,710
Benzyl chloride	4,160	1136.9	3,660
Carbon tetrachloride	2,470	1136.9	2,170

[a] Entire amount retained in the first sorbent tube which contained Tenax GC.

system, of MRC design, was replaced with a Nutech Model 320 Thermal Desorption System. Since the collection tubes used for the ambient air sampler differed from those designed for the Nutech Model 320, an external desorption furnace was connected to the Model 320.

The extremes in humidity presented a problem in the analysis of the Porapak and Ambersorb collector contents. Best results were obtained in previous analyses by maintaining the gas chromatograph column at -30°C during warming of the cryogenic trap. This procedure insured that all trap contents would be on the head of the column before any component began to travel through the column. The large amount of water present in the latter collectors, once condensed, tended to block the column or pass as droplets of water through the column. No data could be obtained under these conditions. By modifying the analytical conditions so that the column was maintained at +30°C during the trap warming cycle, water did not condense and an adequate analysis was possible.

Total ion chromatograms for the Tenax, Porapak and Ambersorb collectors are shown in Figures 37 to 39. Retention values for the various analyses vary because of the change in chromatographic conditions. Components present in the Tenax and Porapak collectors are tabulated and presented in Tables 42 and 43. Note that carbon dioxide appears as two separate peaks in the Porapak sample, and several components such as toluene appear twice. This phenomenon may represent a limitation of the Nutech sample introduction system, with some reconcentrated compounds in the Nutech's trap not introduced into the GC/MS system in a discrete slug.

No component breakthrough into the Ambersorb tubes occurred. The several small peaks which appear in those chromatograms are due to silicone compounds, and are artifacts of the analytical system.

Only benzene and tetrachloroethylene, of the list of twenty potential carcinogens, were detected in the Houston ambient air samples. The distribution of these components between the various sorbents is presented in Table 44.

DISCUSSION

The results presented indicate that components can breakthrough a single Tenax collector under certain conditions. Though all of the factors involved have not been fully defined, it is clear that sampling volume is involved but is not the only factor. Climatic conditions such as temperature and humidity, as well as the composition of the sample, are doubtlessly factors as well. For very low volumes of sample, breakthrough would not be expected. The continually increasing need for lower detection limits, however, requires that a large volume of air be

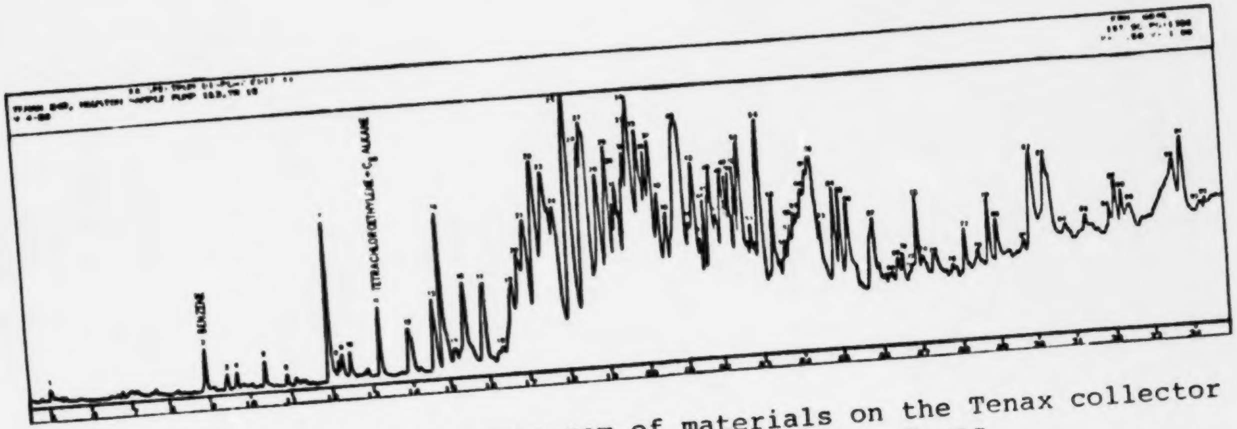


Figure 37. Total ion chromatogram of materials on the Tenax collector after ambient air sampling in Houston, Texas.

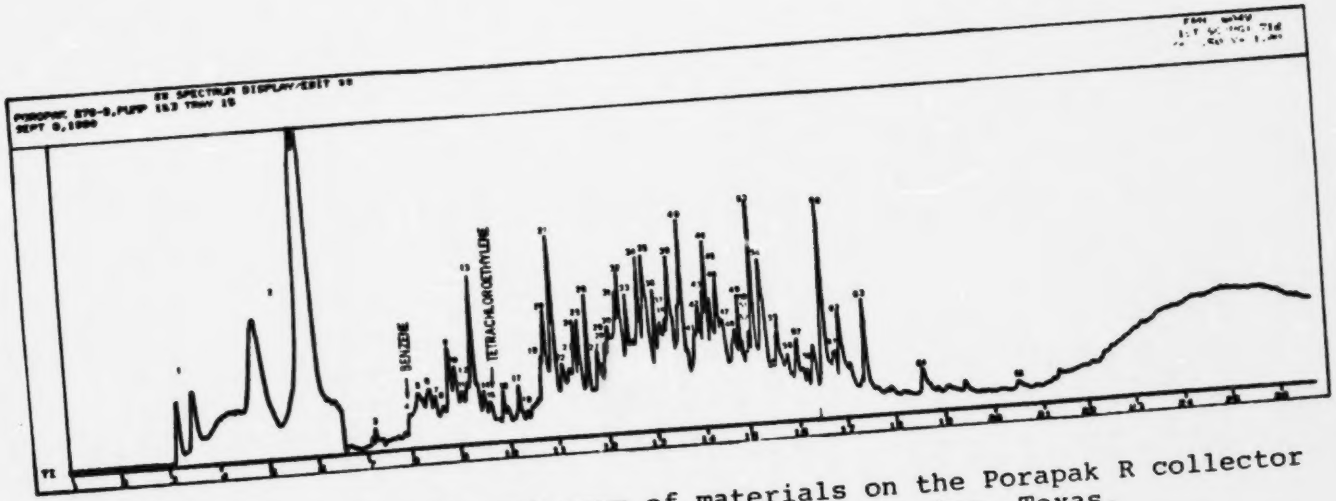


Figure 38. Total ion chromatogram of materials on the Porapak R collector after three-sorbent air sampling in Houston, Texas.

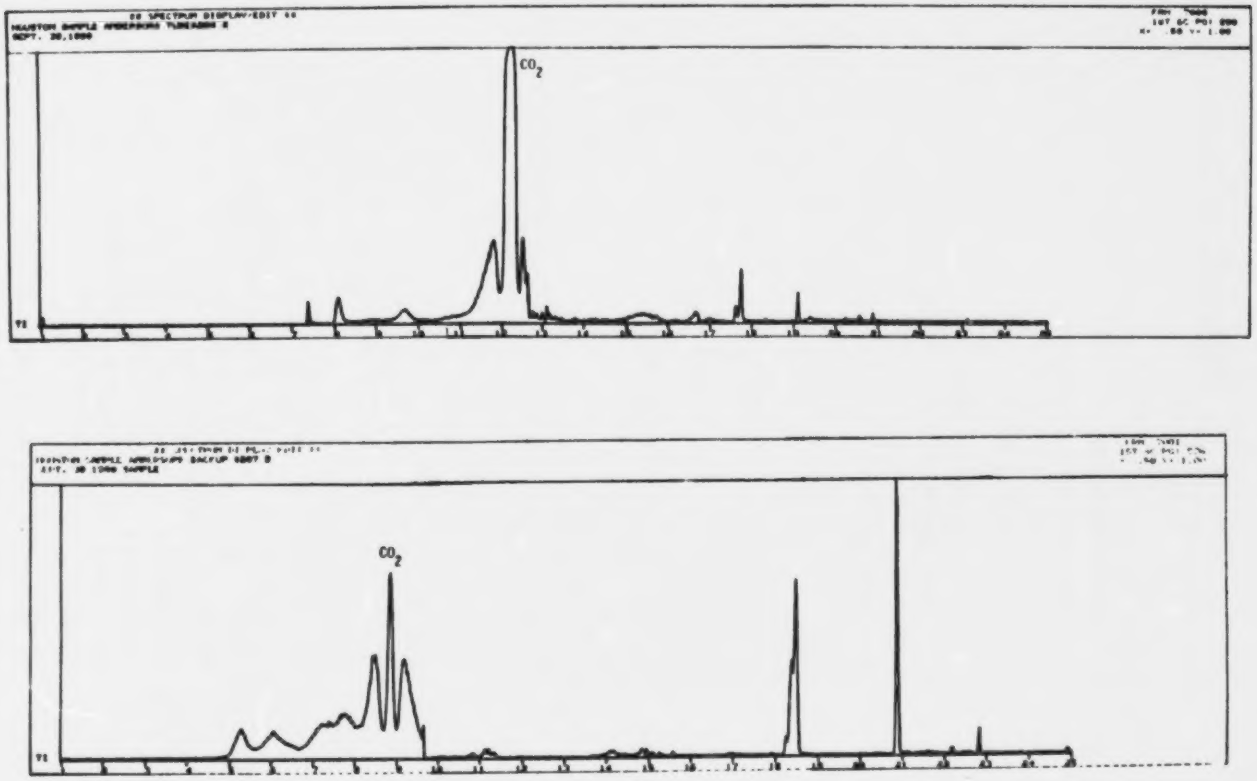


Figure 39. Total ion chromatograms of materials on the Ambersorb collectors after three-sorbent ambient air sampling in Houston, Texas.

TABLE 42. COMPOUNDS COLLECTED ON TENAX GC DURING THREE-SORBENT AIR SAMPLING AT HOUSTON, TEXAS

Chromatographic[a] peak number	Compound
1	Acetone
2	Benzene
3	Trimethylbutane
4	Dimethylpentane
5	Ethylpentane
6	2-Methyl-2-hexene
7	Toluene
8	2,3,4-Trimethylpentane
9	2,3,3-Trimethylpentane
10	3-Ethylhexane
11	Tetrachloroethylene & C_8-Alkane
12	Silicone[b]
13	Ethylbenzene
14	p-Xylene
15	3,4-Dimethylheptane
16	m-Xylene
17	3-Methyl-3-ethylhexane
18	Cumene
19	n-Propylcyclohexane
20	Acetic acid
21	n-Propylbenzene
22	Methylethylbenzene
23	1-Methyl-4-ethylbenzene & 3,4-Diethylhexane
24	3-Ethyl-3-methylheptane
25	1,3,5-Trimethylbenzene
26	3,3-Diethylhexane
27	3-Methylnonane
28	1,2,4-Trimethylbenzene
29	3,3,4,4-Tetramethylhexane
30	n-Decane
31	n-Butylcyclohexane
32	1,3-Diethylbenzene
33	1-Methyl-3-propylbenzene
34	1,3-Dimethyl-5-ethylbenzene
35	1-Methyl-2-propylbenzene
36	1,3-Dimethyl-4-ethylbenzene
37	2-Methyl-1-cyclohexylbutane
38	1,2-Dimethyl-3-ethylbenzene
39	Methylbutylcyclohexane
40	C_{11}-Alkane
41	1,2,3,5-Tetramethylbenzene
42	n-Pentylcyclohexene
43	C_{12}-Alkane
44	C_{12}-Alkane & C_5-Alkylbenzene

(continued)

TABLE 42 (continued)

Chromatographic[a] peak number	Compound
45	C_{12}-Mono-olefin
46	C_{12}-Alkane & C_5-Alkylbenzene
47	1,2,3,4-Tetramethylbenzene
48	C_{12}-Alkane
49	C_5-Alkylbenzene
50	C_{12}-Alkane
51	Alkane
52	Naphthalene
53	1-Methyl-2-pentylcyclohexane
54	C_{12}-Alkane
55	Alkane
56	C_5-Alkylbenzene
57	Benzoic acid
58	Cycloalkane
59	C_6-Alkylbenzene
60	C_6-Alkylbenzene
61	C_6-Alkylbenzene
62	Alkylbenzene(s)
63	Alkane(s)
64	2-Methylnaphthalene
65	C_{13}-Alkane
66	1-Methylnaphthalene
67	Silicone[b]
68	C_{14}-Alkane
69	Biphenyl
70	C_{15}-Alkane
72	Ethylnaphthalene
73	C_{15}-Alkane
74	Dimethylnaphthalene
75	Dimethylnaphthalene
76	Alkane
77	Alkane
78	Alkane
79	Cycloalkane
80	Silicone[b]
81	2-Phenylindole
82	Diethylphthalate
84	Benzophenone
85	Alkane
86	Cycloalkane
87	n-Heptadecane
88	Alkane
89	2-Methoxy-di-t-butylphenol

(continued)

TABLE 42 (continued)

Chromatographic[a] peak number	Compound
90	Anthracene
91	Dibutyl phthalate

[a] Refers to reconstructed total ion chromatogram shown in Figure 37.

[b] Silicone components apparently due to system silanization and/or column bleed.

TABLE 43. COMPOUNDS COLLECTED ON PORAPAK R DURING THREE-SORBENT AIR SAMPLING AT HOUSTON, TEXAS

Chromatographic[a] peak number	Compound
1	Air
2	CO_2
3	Acetaldehyde
4	Benzene & Trimethylbutane
5	Dimethylpentane
6	Ethylpentane
7	2,2,4-Trimethylpentane
8	2,2,3-Trimethylpentane[b]
9	Toluene[b]
10	2,3,4-Trimethylpentane
11	2,2,3-Trimethylpentane[b]
12	3-Ethylhexane
13	Toluene[b]
14	Trimethylpentane
15	Tetrachloroethylene
16	C_8-alkane
17	Silicone[c]
18	2,3-Dimethylheptane
19	Xylene[b]
20	Ethylbenzene
21	Xylene[b]
22	2,3-Dimethylheptane
23	3,4-Dimethylheptane
24	Xylene
25	3-Methyl-3-ethylhexane
26	5-Methyl-2-ethylhexane
27	1-Methyl-2-ethylcyclohexane
28	n-Propylcyclohexane
29	2,2,3-Trimethylheptane
30	C_9-Cycloalkane
31	C_9-Cycloalkanes
32	C_{10}-Alkane
33	C_3-Alkylbenzene
34	3,4-Diethylhexane
35	C_{10}-Alkane
36	3-Ethyl-3-methylheptane
37	C_{10}-Cycloparaffin
38	1,3,5-Trimethylbenzene
39	3,3-Diethylhexane
40	3-Methylnonane
41	1,2,4-Trimethylbenzene & C_{11}-Cycloalkane
42	C_{11}-Alkane
43	4-Methyldecane
44	2-Methyldecane

(continued)

TABLE 43 (continued)

Chromatographic[a] peak number	Compound
45	C_{11}-Alkane
46	Methylbutylcyclohexane
47	C_{11}-Alkane
48	2,2-Dimethylacetylcyclohexane
49	trans-Decalin
50	Alkane
51	C_4-Alkylbenzene
52	Alkane
53	o-Ethylstyrene
54	p-Ethylstyrene
55	C_{11}-Alkane
56	Diethylphenol
57	2-Methyl-trans-decalin
58	Alkane
59	2-Methyl-cis-decalin
60	Vinylphenylcarbinol
61	Dimethylindan
62	Ethylbenzaldehyde
63	Alkane
64	Ethylacetophenone
65	Alkane

[a] Refers to reconstructed total ion chromatogram shown in Figure 38.

[b] Apparent doubling of peaks due to uneven trap warming phenomenon.

[c] Silicone components apparently due to system silanization and/or column bleed.

TABLE 44. SUBJECT COMPOUNDS PRESENT IN SAMPLES COLLECTED IN HOUSTON, TEXAS

Compound	Weight per collector, ng			Total weight, ng	Concentration,[a] ng/m^3 in air
	Tenax-GC	Porapak R	Ambersorb		
Benzene	151	55	-	206	450
Tetrachloroethylene	34	1	-	35	76

[a] 461 liters of air sampled.

sampled to assure sufficient material for analyses. The data obtained during the Niagara Falls sampling shows that, even with a large volume, Tenax may retain all of the organic constituents under certain conditions. The sample volume taken at that location was greater than that taken during Houston sampling and nearly as great as that taken at Los Angeles. Moreover, the loading of the specific compounds of interest was greater than that found at the other locations.

Compound retention on Tenax sorbent may be affected by other factors, the evaluation of which is beyond the scope of this program. These may include selective displacement effects by other matrix compounds; interaction with water whereby an immiscible compound pair, having a combined vapor pressure higher than that of either compound (as in steam distillation) is formed; change in the surface characteristics of the Tenax due to atmospheric constituents such as ozone or NO_x.

Except under certain very controlled or specific conditions the multisorbent sampling approach is required to assure complete retention of all compounds.

The methodology developed during the course of this program has been applied to a wide variety of potential carcinogens to demonstrate its effectiveness as a screening technique. As noted previously, certain artifact compounds have been found in most of the samples. Some of these, such as the silicones, are recognized as originating from the analytical system. Great importance has been placed on the recognition of artifact peaks only if the compound is environmentally significant.

SECTION 11

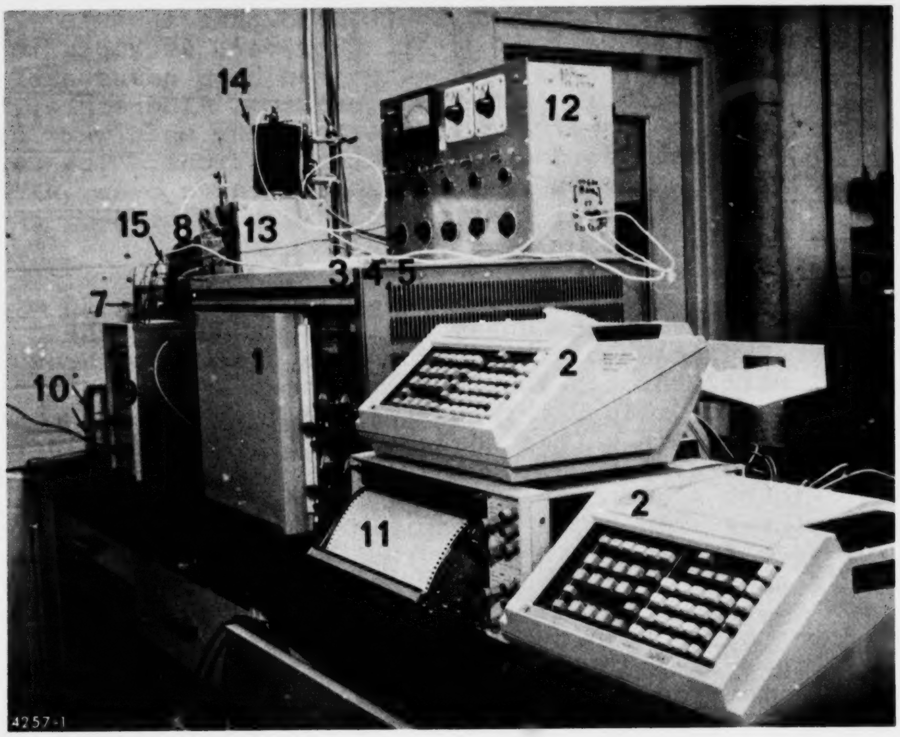
ANALYSIS OF FIELD SAMPLES BY MULTI-DETECTOR CAPILLARY GAS CHROMATOGRAPHY

OBJECTIVE

The non-specificity of conventional gas chromatographic (GC) analyses has traditionally been a major drawback of the technique. This has led to the heavy dependence on gas chromatography/mass spectrometry (GC/MS) as the technique for accomplishing unequivocal identification of compounds. However, certain GC detectors (e.g., electron capture, photoionization, nitrogen-phosphorus specific flame ionization) offer degrees of selectivity for certain compounds that have potential for decreasing the dependence on GC/MS. If operated simultaneously during an analysis, this permits the ratioing of different detector responses for compounds "seen" by more than one detector. When used in conjunction with GC retention times, detector response ratios provide an additional parameter which greatly improve the confidence of compound specificity of a GC analysis. The objective of this work was to conduct a preliminary investigation of multiple selective detection and detector response ratioing as an alternative technique to mass spectrometry for the detection of the compounds of interest. This investigation was to include analyses of "field" samples and a comparison of multi-detector capillary GC results with mass spectrometric results obtained for comparable "field" samples.

INSTRUMENTATION

A multi-detector capillary gas chromatographic [MD(GC)^2] system developed through independent research at Monsanto Research Corporation was used to evaluate the applicability of this analytical technique for this program. This system is shown in Figure 40. It consisted of a Hewlett-Packard Model 5880 gas chromatograph with dual printer/ plotters, three installed detectors [electron capture (ECD), flame ionization (FID), and NP-flame ionization (NPD)], dual computer interface boards, one analog output board (installed during the course of these evaluations), dual capillary injection ports, and a heated collection vent. Each of the three installed detectors had independent supplies of makeup carrier gases. Mounted to the side of the GC, at the heated collection vent, was a HNU Inc. Model PI-52 photoionization detector (PID). The PID was controlled by a power supply/electrometer unit. Signals from the PID electrometer and



1 - HP MODEL 5880 GC
2 - PRINTER/PLOTTERS
3 - NP-FID
4 - FID
5 - ECD
6 - PID AND HEATED COLLECTION VENT
7 - PID POWER SUPPLY/ELECTROMETER
8 - HALL ELECTROLYTIC DETECTOR
9 - HALL POWER SUPPLY/ELECTROMETER
10 - HP A/D CONVERTERS
11 - HP STRIP CHART RECORDER
12 - CAPILLARY INLET SYSTEM THERMAL CONTROLLER
13 - CAPILLARY INLET SYSTEM VALVE OVEN
14 - CAPILLARY INLET SYSTEM DESORPTION CHAMBER
15 - CAPILLARY INLET SYSTEM TRAP

Figure 40. Multi-detector, capillary gas chromatograph.

the GC analog output board were plotted on a Hewlett-Packard Model 7132A dual pen strip chart recorder and monitored by computer through Hewlett-Packard Model 18652A analog to digital (A/D) converters. A Tracor Model 700 Hall electrolytic conductivity detector was mounted above the PID so that the PID effluent would be passed to the Hall detector. However, attempts to detect compounds with the Hall detector had been unsuccessful with the MD(GC)^2 system in this configuration. Therefore, the Hall detector and its power supply/electrometer unit were disconnected and not used during these determinations. The capillary inlet system, with desorption chamber, valve oven, nickel capillary trap, and thermal control unit were mounted on top of the GC.

A Hewlett-Packard, OV-101 WCOT, fused-silica column (∿25 m long, ∿0.3 mm ID) was used as the analytical column during these evaluations. The inlet of this column was passed up through the GC injection port, through the injection port septum, and directly connected to the capillary inlet system valve. Small exposed portions of the column were ensheathed in 1.6 mm (1/16 in.) OD nickel tubing and wrapped with glass wool to ensure good heat transfer. Figure 41 depicts a schematic of gas flows through the capillary inlet system. The GC capillary carrier shown in this schematic was obtained by inserting a 1.6 mm (1/16 in.) stainless steel tee in the injection port carrier gas supply line immediately prior to the GC injection port. One arm of the tee was capped and the other connected to the capillary inlet system. (Other gas lines to the GC injection port were also capped to prevent contamination of the GC.) The other end of the analytical capillary column was connected to a 1.6 mm (1/16 in.) stainless steel union with a nut and graphite ferrule. Four ∿30 cm lengths of fused-silica columns were attached to the other end of the union with a vent and specially formed graphite-ribbon ferrule. Two of these lengths were ∿0.3 mm ID, OV-101 WCOT column pieces and were connected to the PID and NP-FID. The other two lengths were ∿0.2 mm ID, OV-101 WCOT column pieces and were connected to the ECD and FID. A photograph of the GC oven is given in Figure 42.

The MD(GC)^2 system was interfaced to a Hewlett-Packard Model 3354 laboratory automation system. Prior to receiving the GC analog output board, the system's detectors were monitored as described below:

- The PID signal was plotted on the strip chart recorder and monitored by the computer with an A/D converter.
- The NP-FID signal was plotted on a printer/plotter but was not monitored by the computer (i.e., plot only).
- The FID signal was plotted on the other printer/plotter and monitored by the computer through one of the GC's computer interface boards.

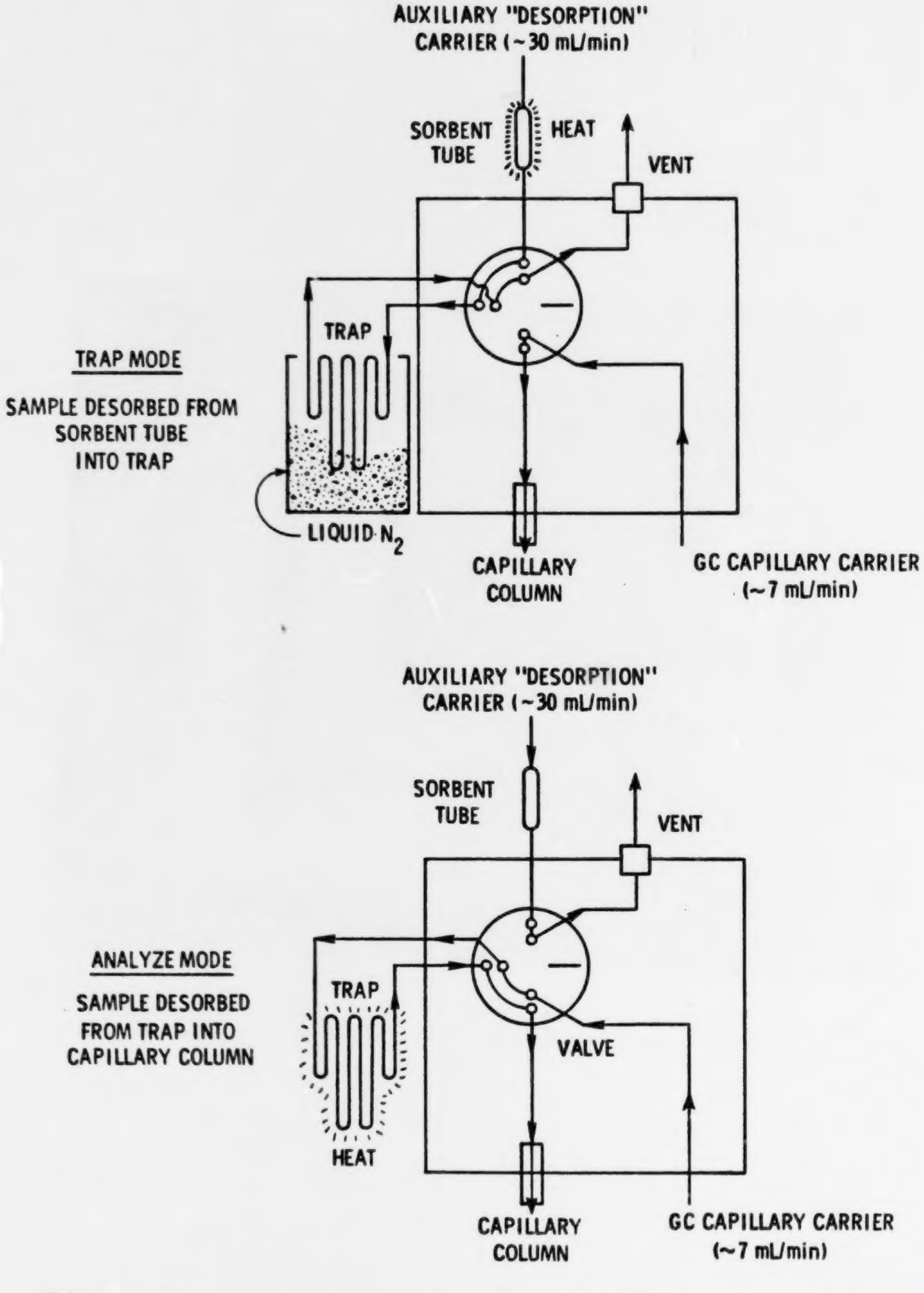

AUXILIARY "DESORPTION" CARRIER (~30 mL/min)
SORBENT TUBE
HEAT
VENT
TRAP
TRAP MODE
SAMPLE DESORBED FROM SORBENT TUBE INTO TRAP
LIQUID N2
CAPILLARY COLUMN
GC CAPILLARY CARRIER (~7 mL/min)
AUXILIARY "DESORPTION" CARRIER (~30 mL/min)
SORBENT TUBE
VENT
ANALYZE MODE
SAMPLE DESORBED FROM TRAP INTO CAPILLARY COLUMN
TRAP
VALVE
HEAT
CAPILLARY COLUMN
GC CAPILLARY CARRIER (~7 mL/min)

Figure 41. Flow schematic of capillary inlet system.

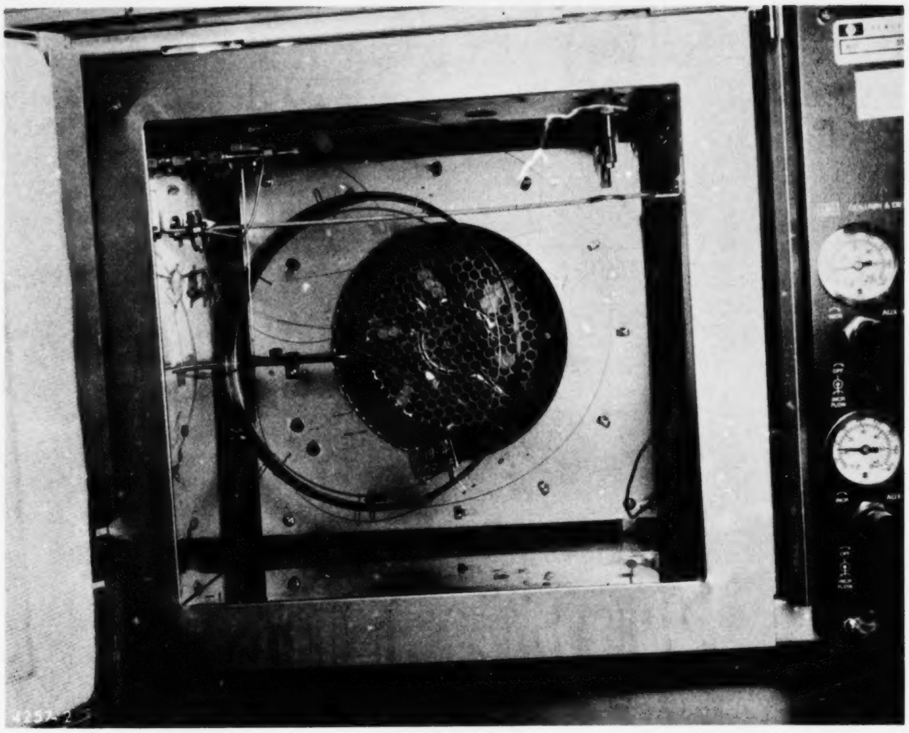


Figure 42. Gas chromatograph oven with fused-silica capillary column split to four detectors.

- The ECD signal was not plotted but was monitored by the computer through the other GC computer interface board (i.e., computer only).

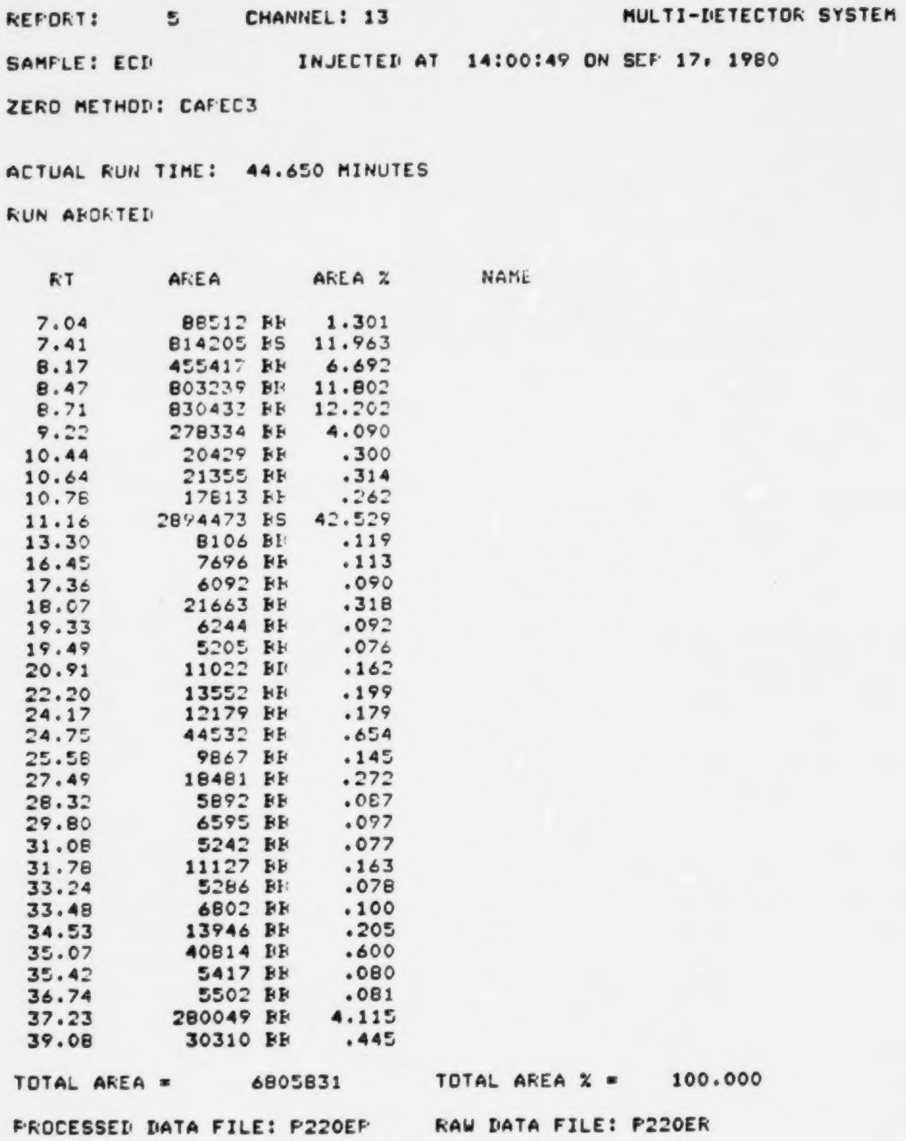
Signals monitored by the computer were integrated and the results obtained from a Decwriter III Model LS-120 high speed terminal. Figure 43 gives an example of a typical computer report. The signals were also recorded and stored on the computer's disc. Chromatograms could be reconstructed from this stored information on a Tektronix Model 4010-1 cathode ray tube (CRT) terminal and printed by a Tektronix Model 4610 hard copy unit. After obtaining the GC analog output board the following changes were made in how the detectors were monitored.

- The NP-FID signal was outputted through the analog output board, plotted on the strip chart recorder, and monitored by the computer with an A/D converter.
- The ECD signal was plotted on a printer/plotter and monitored by the computer through a GC computer interface board.
- The PID and FID signals were monitored as described previously.

RESULTS

A number of analyses were performed using the MD(GC)^2 system with the chromatographic conditions given in Table 45. The only variations in these conditions were the changes in the computer interfacing, previously described, and a change in the level 2 program rate (from 8°C/min to 3°C/min) for the analysis of Tenax tube #271 and one standard mixture.

One set of field sample tubes were analyzed, excluding the Ambersorb backup tube, on the MD(GC)^2 system. This sample was collected in Houston, Texas, on 30 July 1980 with the ambient air collection system. The chromatograms obtained for this set of tubes are depicted in Figures 44, 45, and 46 for the Tenax, Porapak R, and Ambersorb tubes, respectively. These chromatograms, except for the Tenax and Ambersorb NP-FID tracers, are computer reconstructed. They are normalized with the largest peaks at full-scale and with the same time scale. Much chromatographic resolution is lost by the reconstruction process but this doesn't affect computer integration. The two NP-FID traces were obtained from a printer/plotter. Note that the Tenax traces indicate most of the higher molecular weight compounds collected on this sorbent tube, while only the most volatile compounds are indicated as being collected by the Ambersorb tube. For the Porapak R and Ambersorb tubes the first peaks eluting after temperature programming was initiated



```
REPORT:     5     CHANNEL: 13                  MULTI-DETECTOR SYSTEM

SAMPLE: ECD             INJECTED AT  14:00:49 ON SEP 17, 1980

ZERO METHOD: CAPEC3

ACTUAL RUN TIME:  44.650 MINUTES

RUN ABORTED

   RT          AREA        AREA %         NAME

   7.04        88512 BB    1.301
   7.41       814205 BS   11.963
   8.17       455417 BB    6.692
   8.47       803239 BB   11.802
   8.71       830433 BB   12.202
   9.22       278334 BB    4.090
  10.44        20429 BB     .300
  10.64        21355 BB     .314
  10.78        17813 BB     .262
  11.16      2894473 BS   42.529
  13.30         8106 BB     .119
  16.45         7696 BB     .113
  17.36         6092 BB     .090
  18.07        21663 BB     .318
  19.33         6244 BB     .092
  19.49         5205 BB     .076
  20.91        11022 BV     .162
  22.20        13552 BB     .199
  24.17        12179 BB     .179
  24.75        44532 BB     .654
  25.58         9867 BB     .145
  27.49        18481 BB     .272
  28.32         5892 BB     .087
  29.80         6595 BB     .097
  31.08         5242 BB     .077
  31.78        11127 BB     .163
  33.24         5286 BB     .078
  33.48         6802 BB     .100
  34.53        13946 BB     .205
  35.07        40814 DB     .600
  35.42         5417 BB     .080
  36.74         5502 BB     .081
  37.23       280049 BB    4.115
  39.08        30310 BB     .445

 TOTAL AREA =      6805831        TOTAL AREA % =     100.000

 PROCESSED DATA FILE: P220EP      RAW DATA FILE: P220ER
```

Figure 43. Computer printout of computer integrated chromatographic data from the analysis of Porapak R tube #220 with electron capture detection.

TABLE 45. CHROMATOGRAPHIC CONDITIONS

Parameter		Value	Parameter		Value
GC zone temperatures:	Detector zone 1 (NP-FID)	300°C	Capillary inlet system:	Valve temperature	∿220°C
	Detector zone 2 (FID & ECD)	300°C		"Trap" loop temperature	Liq N_2
	Injection port zone 1	250°C		"Analyze" loop temperature	∿200°C
	Auxiliary zone 1 (to PID)	250°C		Loop purge time	5 min
GC oven temperature program:				Desorption temperature	200°C,[a] 300°C[b]
	Initial equilibration time	1 min		Desorption time	35 to 40 min
	Initial value	-30°C	Carrier gas:	Type	Helium
	Initial time	5 min		Tank pressure	60 psi
	Level 1 program rate	30°C min		Column back pressure	20 psi
	Level 1 final value	0°C		Column flow rates	∿7 mL/min
	Level 1 final time	0 min			
	Level 2 program rate	8°C/min	FID makeup gas:	Type	Helium
	Level 2 final value	250°C		Tank pressure	60 psi
	Level 2 final time	20 min		GC pressure	12 psi
GC capillary injection mode		Splitless		Flowrate	∿30 mL/min
GC terminal 1:	Plotter signal	FID	NP-FID makeup gas:	Type	Helium
	Plotter chart speed	0.5 cm/min		Tank pressure	60 psi
GC terminal 2:	Plotter signal	ECD		GC pressure	10 psi
	Plotter chart speed	0.5 cm/min		Flow rate	∿17 mL/min
GC A/D loop board 1:	Signal	FID	PID makeup gas:		none
	Channel	12	ECD makeup gas:	Type	Arg/meth (5%)[c]
GC A/D loop board 2:	Signal	ECD		Tank pressure	50 psi
	Channel	13		GC pressure	20 psi
				Flow rate	∿30 mL/min
GC D/A board:	Signal	NP-FID			
A/D Converter:	Signal	NP-FID	Detector gas:	Type	Air
	Channel	11		Tank pressure	40 psi
A/D Converter:	Signal	PID		GC pressure	30 psi
	Channel	10		FID flow rate	∿400 mL/min
				NP-FID flow rate	∿55 mL/min
Strip chart recorder:	Chart speed	6.4 mm/min (0.25 in./min)	Detector gas:	Type	Hydrogen
				Tank pressure	40 psi
	Pen #1 signal	PID		GC pressure	30 psi
	Pen #1 and #2 range	10 mV		FID flow rate	∿30 mL/min
	Pen #2 signal	NP-FID		NP-FID flow rate	∿4 mL/min
PID power supply/ electrometer:	Detector temperature	∿230°C			
	Input attenuation	10^{-11} Amps			
	Recorder output polarity	Positive			
	Lamp intensity	5.1 marks			

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[a] For desorption of Porapak R tubes.

[b] For desorption of Tenax and Ambersorb tubes.

[c] 5% methane in argon.

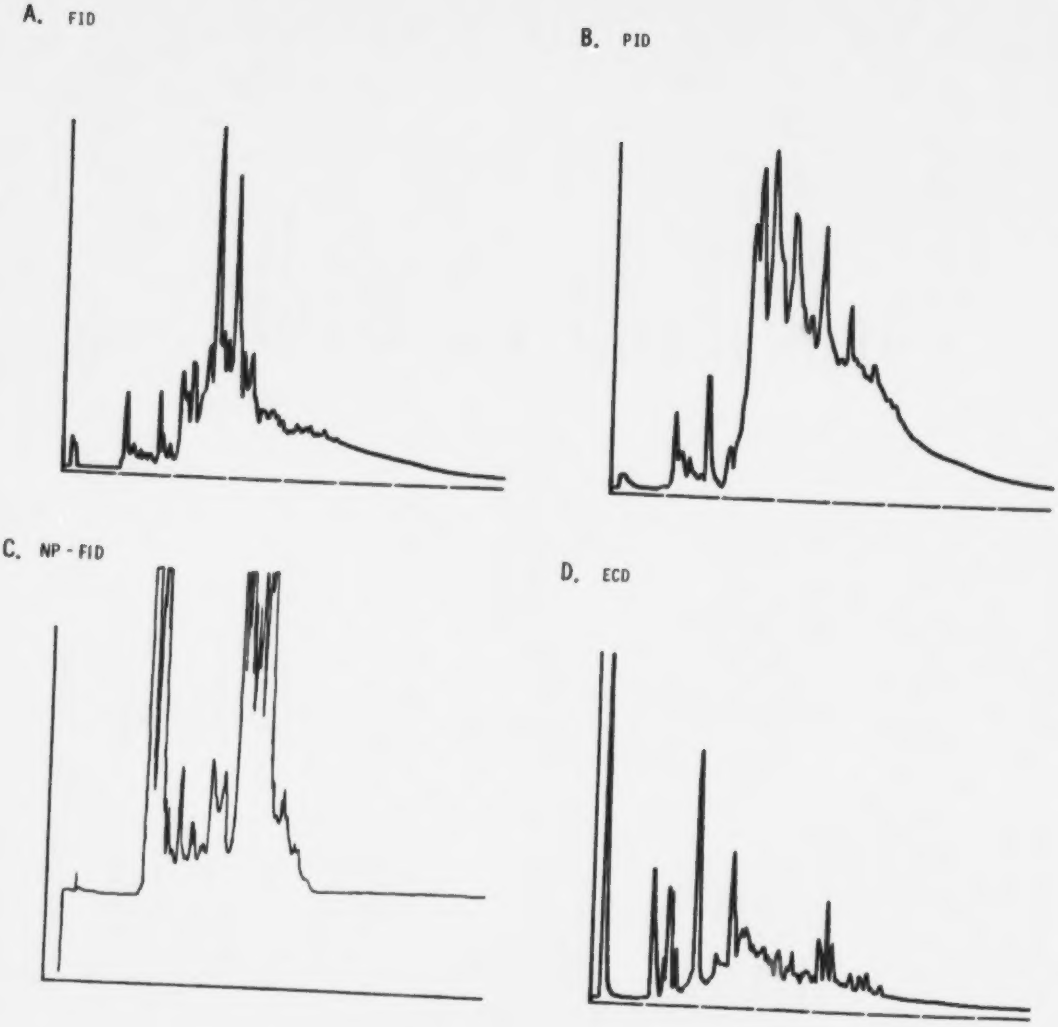

Figure 44. Analysis of Tenax tube #236, a Houston air sample.

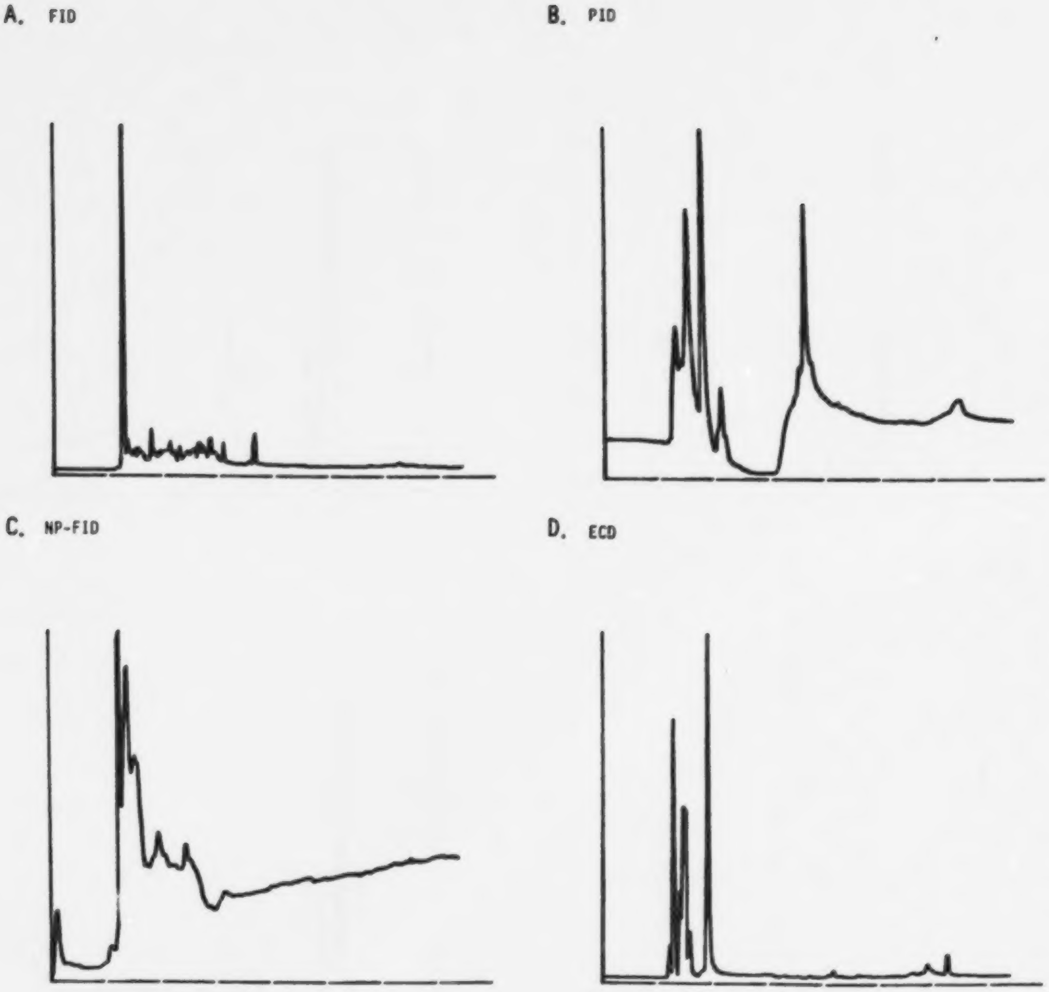

Figure 45. Analysis of Porapak R tube #220, a Houston air sample.

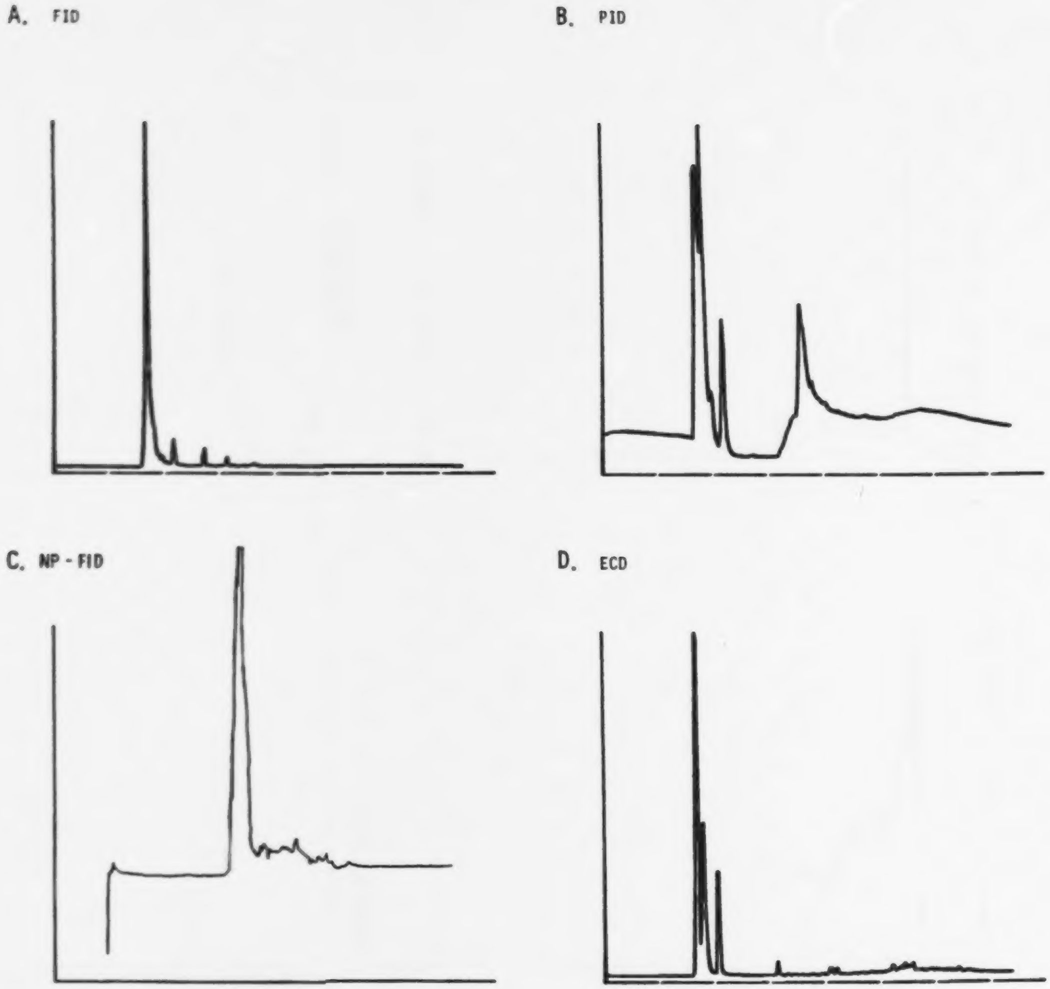

Figure 46. Analysis of Ambersorb XE-340 tube #272, a Houston air sample.

were later than those for the Tenax tube. This was possible due to a "solvent effect" created by large amounts of water in the Porapak R and Ambersorb tubes.

Qualitative standard mixtures were prepared by putting ∿10 mg (i.e., ∿1 drop) of each mixture component into ∿10 mL of solvent. One mixture contained benzene, carbon tetrachloride, acrolein, acrylonitrile, vinyl acetate, styrene, ethylene dichloride, ethylene dibromide, tetrachloroethylene, cis-1,3-dichloropropene, trans-1,3-dichloropropene, and 1,4-dioxane in n-tridecane. A typical analysis of this mixture on the MD(GC)^2 system is shown in the chromatograms in Figure 47. A similar mixture was prepared containing toluene-2,4-diamine, benzyl chloride, hexachloro-1,3-butadiene, and di-(2-ethylhexyl) phthalate in methanol. These qualitative standards were used to establish retention time ranges, detector responses, and detector response ratios for compound identification. The results for a number of these standards are compiled in Table 46.

Integration data from computer reports for sorbent tube analyses were evaluated in comparison to the results of the standard mixtures. An example of how these data were evaluated is given in Table 47. Detector responses within the retention time ranges of the compounds of interest were noted for each detector. The retention times and areas of those responses were recorded beside the compounds of interest in a table. Responses of different detectors with close retention times were placed beside each other and considered simultaneous responses to the same peak. Determination of simultaneous responses was a subjective evaluation. Allowances were made for differences in retention times due to offset in computer integration and due to differences in detector response intensities. The pattern of detector responses was then noted for all simultaneous responses, and response ratios were calculated as required, Simultaneous responses were then assigned points according to the criteria given at the end of Table 47. One mandatory criterion had to be met: the detector responses had to be the correct pattern, or no points were assigned. Responses potentially positively identifying the compound of interest were then flagged with an asterisk. If more than one group of simultaneous responses occurred within the retention time ranges of some compounds, the group most likely to indicate that compound was subjectively determined. The number of points assigned, closeness to the retention time optimum, and potential identifications of other compounds were among the factors considered. Tables of this type were prepared for each analysis evaluated.

A compilation of results is given in Table 48. All compounds flagged as being potentially positively identified are indicated by the presence of FID retention times under the appropriate analysis. The number of assigned points are then compared to the total number possible and the percentage calculated. This

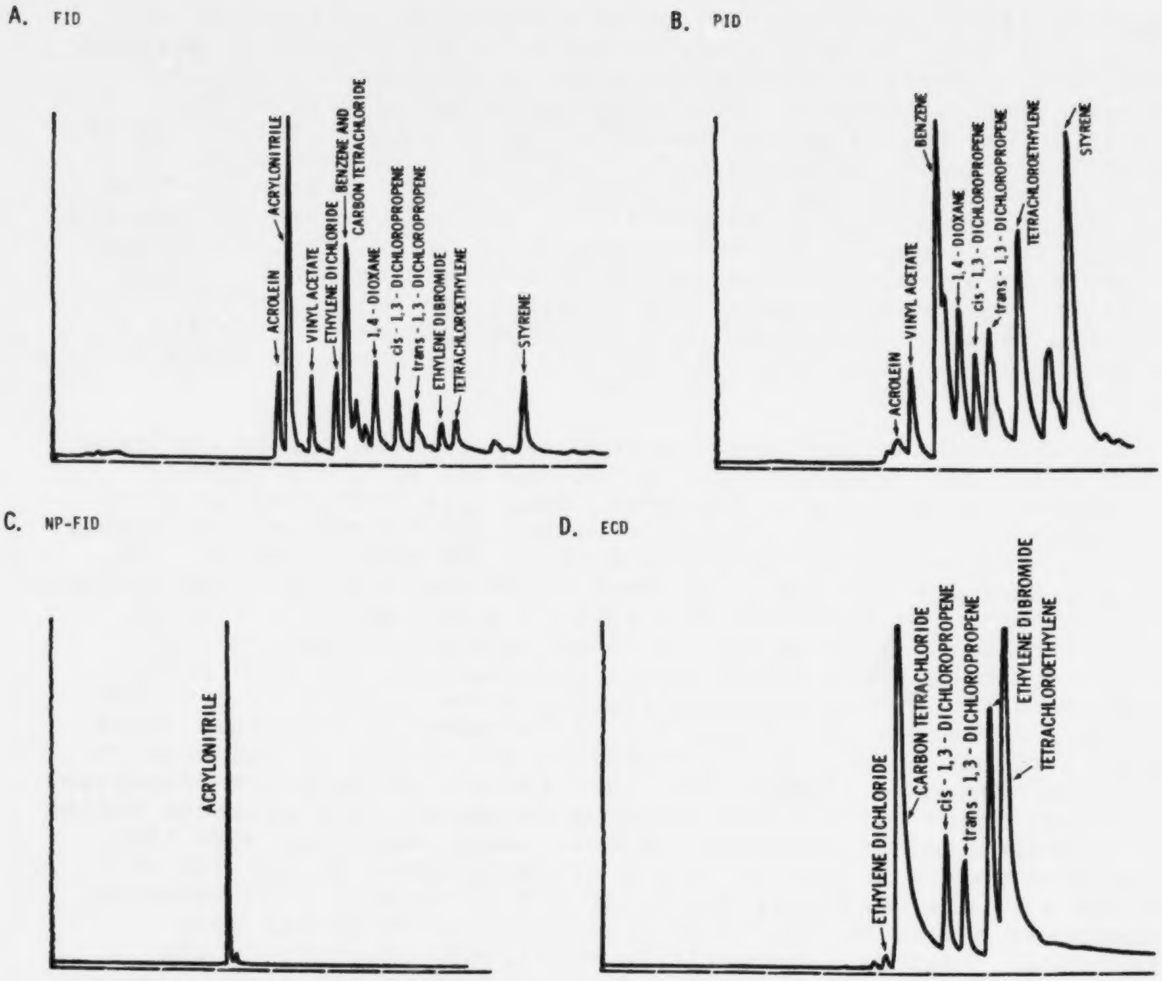

Figure 47. Multi-detector $(GC)^2$ analysis of a standard mixture of acrolein, acrylonitrile, vinyl acetate, ethylene dichloride, benzene, carbon tetrachloride, 1,4-dioxane, cis-1,3-dichloropropene, trans-1,3-dichloropropene, ethylene dibromide, tetrachloroethylene, and styrene in n-tridecane.

TABLE 46. COMPILATION OF RESULTS FOR ANALYTICAL STANDARDS

Compound	Retention time, min		Responses				Response ratios					
	Range	Optimum	FID	ECD	PID	NPD	ECD/FID	PID/FID	ECD/PID	NPD/FID	ECD/NPD	NPD/FID
Acrolein	5.6-6.6	6.09-6.11	+	0	+	0		1/1.23				
Acrylonitrile	5.9-6.9	6.38-6.39	+	0	0	+				31.7/1		
Vinyl acetate	6.5-7.5	6.96-7.02	+	0	+	0		3.76/1				
Ethylene dichloride	7.2-8.2	7.69-7.71	+	+	0	-	10.2/1					
Benzene	7.4-8.5	7.93-8.02	+	0	+	0		8.17/1				
							(410/1[a])	(3.38/1[a])	(115/1[a])			
Carbon tetrachloride	7.4-8.5	7.93-8.02	+	0	+	0	1321/1					
1,4-Dioxane	8.2-9.3	8.73-8.80	+	0	+	0		3.40/1				
cis-1,3-Dichloroprene	8.8-9.9	9.34-9.41	+	+	+	-	131/1	3.24/1	46.6/1			
trans-1,3-Dichloropropene	9.3-10.4	9.85-9.93	+	+	+	-	127/1	5.37/1	27.7/1			
Ethylene dibromide	10.1-11.1	10.60-10.63	+	+	0	-	798/1					
Tetrachloroethylene	10.4-11.5	10.93-11.01	+	+	+	-	1938/1	20.2/1	117/1			
Styrene	12.2-13.3	12.70-12.79	+	0	+	0		9.99/1				
Toluene-2,4-diamine[b]	14.1-15.4	14.60-14.90	+	+	+	+	90.4/1	8.20/1	15.9/1	NE	NE	NE
Hexachloro-1,3-butadiene	19.0-20.2	19.47-19.69	+	+	+	0	1528/1	23.5/1	64.9			
Benzyl chloride	21.0-22.3	21.65-21.74	+	+	+	0	5.94/1	3.02/1	1/5.94			
Di-(2-ethylhexyl) phthalate	24.8-26.2	25.33-25.71	+	+	+	0	10.2/1	63.5/1	1/6.50			
Ethylene glycol[c,d]	NE[e]	NE	ND[f]	ND[f]	ND	NE						
Pentachlorophenol[d]	NE	NE	+	+	0	NE	1098/1					
Benzidine[d]	NE	NE	+	+	0	NE	1/6.7					
Chrysene[d]	NE	NE	+	-	0	NE						
Benzo(a)pyrene[d]	NE	NE	+	-	0	NE						

---

[a] For co-eltuing peaks.

[b] Not evaluated with computer integration of NP-FID.

[c] Dimer of ethylene oxide; not detected at all, probably decomposed.

[d] Not evaluated with appropriate chromatographic conditions.

[e] Not evaluated.

[f] Not detected.

KEY FOR RESPONSES:

+ Positive response
- Negative response
0 No detectable response

TABLE 47. EVALUATION OF RAW DATA OF PORAPAK R TUBE #220 ANALYSIS

		Flame ionization		Electron capture		Photoionization		Nitrogen/ Phosphorus		Responses				Response ratios					
Compound	Retention time range, min	RT,^{a} min	Area, counts^{b}	RT,^{a} min	Area, counts^{b}	RT,^{a} min	Area, counts^{b}	RT,^{a} min	Area, counts^{b}	FID^{c}	ECD^{d}	PID^{e}	NPD^{f}	ECD/ FID	PID/ FID	ECD/ PID	NPD/ FID	ECD/ NPD	Points^{g}
Acrolein	5.6 - 6.6 (6.09-6.11)^{h}	6.67	3,476																
Acrylonitrile	5.9 - 6.9 (6.38-6.39)	6.67	3,476			6.85	1,545												
		6.95	3,333																
Vinyl acetate	6.5 - 7.5 (6.96-7.02)	6.67	3,476			6.85	1,545												
		6.95 7.04	3,333 2,353	7.04	88,512					+	+	0	0	37.6 /1					
		7.11 7.20 7.23 7.27^{i}	5,529 112,579 684,433 6,391			7.28^{i}	22,992			+	0	+	0		3.60 /1				3^{i}
		7.30 7.32 7.38	6,142 5,462 26,181	7.41	814,205			7.35	2,778	+	+	0	+	31.1 /1			1/ 9.42	293 /1	3
		7.46	10,590			7.47	55,033			+	0	+	0		5.20 /1				
		7.53	402																
Ethylene dichloride	7.2 - 8.2 (7.69-7.71)	7.20 7.23 7.27	112,579 684,433 6,391			7.28	22,992			+	0	+	0		3.60 /1				
		7.30 7.32 7.38	6,142 5,462 26,181	7.41	814,205			7.35	2,778	+	+	0	+	31.1 /1			1/ 9.42	293 /1	
		7.46	10,590			7.47	55,033			+	0	+	0		5.20 /1				
		7.53 7.62 7.84	402 643 21,672			7.80	18,172			+	0	+	0		1/ 1.19				
		7.95	14,597			7.97	18,408			+	0	+	0		1.26 /1				
		8.13	18,118	8.17	455,417	8.14	48,610			+	+	+	0	25.1 /1	2.68 /1	9.37 /1			
								8.24	25,118										
Benzene and carbon tetrachloride	7.4 - 8.5 (7.93-8.02)	7.38	26,181	7.41	814,205			7.35	2,778	+	+	0	+	31.1 /1			1/ 9.42	293 /1	3
		7.46	10,590			7.47	55,033			+	0	+	0		5.20 /1				
		7.53 7.62 7.84	402 643 21,672			7.80	18,172			+	0	+	0		1/ 1.19				3
		7.95	14,597			7.97	18,408			+	0	+	0		1.26 /1				5
		8.13^{i}	18,118	18.17^{i}	455,417	8.14^{i}	48,610			+	+	+	0	25.1 /1	2.68 /1	9.37 /1			5½^{i}
								8.24	25,118										
		8.37 8.45	7,598 5,379	8.47	803,239					+	+	0	0	149 /1					4

TABLE 47 (continued)

Compound	Retention time range, min	Flame ionization		Electron capture		Photoionization		Nitrogen/ Phosphorus		Responses				Response ratios					Points[g]
		RT,[a] min	Area counts[b]	RT,[a] min	Area counts[b]	RT,[a] min	Area counts[b]	RT,[a] min	Area counts[b]	FID[c]	ECD[d]	PID[e]	NPD[f]	ECD/ FID	PID/ FID	ECD/ PID	NPD/ FID	ECD/ NPD	
1,4-Dioxane	8.2 - 9.3							8.24	25,118										
	(8.73-8.80)	8.37	7,598																
		8.45	5,379	8.47	803,239					+	+	0	0	149 /1					
		8.66[i]	17,747			8.63[i]	48,275			+	0	+	0		2.69 /1				4[i]
				8.71	830,433	8.72	90,408			0	+	+	0			9.19 /1			
		8.76	5,001																
		8.78	8,657																
		8.96	17,850																
								9.01	14,621										
		9.07	17,419																
		9.24	16,838	9.22	278,334	9.20	46,405			+	+	+	0	16.5 /1	2.76 /1	6.00 /1			
cis-1,3-Dichloro-propene	8.8 - 9.9	8.76	5,001																
	(9.34-9.41)	8.78	8,657																
		8.96	17,850																
								9.01	41,621										
		9.07	17,419																
		9.24[i]	16,838	9.22[i]	278,334	9.20[i]	46,405			+	+	+	0	16.5 /1	2.76 /1	6.00 /1			3½[i]
		9.46	11,156																
						9.63	23,411												
		9.69	7,971																
		9.91	1,974			9.95	14,494			+	0	+	0		7.34 /1				
trans-1,3-Dichloro-propene	9.3 - 10.4	9.46	11,156																
	(9.85-9.93)					9.63	23,411												
		9.69	7,971																
		9.91	1,974			9.95	14,494			+	0	+	0		7.34 /1				
		10.02	9,533																
						10.29	163,490												
		10.34	60,398																
				10.44	20,429														
Ethylene dibromide	10.1 - 11.1					10.29	163,490												
	(10.60-10.63)	10.34	60,398																
				10.44	20,429														
		10.66[i]	39,489	10.64[i]	21,355					+	+	0	0	1/ 1.85					3[i]
		10.79	25,038	10.78	17,813					+	+	0	0	1/ 1.41					2
		11.00	12,180					11.03	163	+	0	0	+						
		11.07	10,776																
Tetrachloro-ethylene	10.4 - 11.5			10.44	20,429														
	(10.93-11.01)	10.66	39,489	10.64	21,355														
		10.79	25,038	10.78	17,813														
		11.00	12,180					11.03	163	+	0	0	+				1/ 74.7		
		11.07	10,776																
				11.16	2,894,473														
		11.33	35,121																
								11.49	1,782										

TABLE 47 (continued)

Compound	Retention time range, min	Flame ionization		Electron capture		Photoionization		Nitrogen/ Phosphorus		Responses				Response ratios					Points[g]
		RT,[a] min	Area,[b] counts	RT,[a] min	Area,[b] counts	RT,[a] min	Area,[b] counts	RT,[a] min	Area,[b] counts	FID[c]	ECD[d]	PID[e]	NPD[f]	ECD/ FID	PID/ FID	ECD/ PID	NPD/ FID	ECD/ NPD	
Styrene	12.2 - 13.3					12.16	7,418	12.23	348	+	0	0	+				1/ 78.9		
	(12.70-12.79)	12.22	27,468																
						12.37	24,250												
		12.43	47,067																
		12.72	12,141																
						12.78	12,749												
		12.85	24,644																
		13.01	14,511																
				13.30	8,106														
						13.38	1,457												
						14.12	291												
Toluene-2,4-diamine	14.1 -15.4																		
	(14.60-14.90)	14.20	27,727																
		14.32	29,264			14.30	812			+	0	+	0		1/ 36.0				
								14.51	1,552										
		14.59	22,388																
		14.83	40,930																
						14.97	97												
		15.04	60,899																
		15.28	9,977																
		15.39	10,956																
Hexachloro-1,3-butadiene	19.0 - 20.2	19.27	1,014																
	(19.47-19.69)			19.33	6,244														
				19.49	5,205														
		20.11	1,292																
Benzyl chloride	21.0 - 22.3	20.95	15,157																
	(21.65-21.74)					21.47	155,133												
		21.56	73,423																
		22.20[i]	2,139	22.20[i]	13,552	22.24[i]	135,723			+	+	+	0	6.34 /1	63.5 /1	1/ 10.0			3½[i]
Di-(2-ethylhexyl) phthalate	24.8 - 26.2			24.75	44,532														
	(25.33-25.71)					25.06	41,265												
				25.58	9,867														
						25.64	8,092												
						25.75	10,270												
						25.94	81,156												

Criteria	Points
Correct combination of responses within RT range[j]	+1
RT within optimum RT range.	+2
RT within 0.2 min of optimum RT range	+2
For peaks with one response ratio:	
Response ratio within an order of magnitude in 0.1 to 100 range, and within two orders of magnitude in ≥1,000 range.	+1
Response ratio not within above criteria.	+0
For peaks with more than one response ratio:	
Response ratio within an order of magnitude in 0.1 to 100 range, and within two orders of magnitude in ≥1,000 range.	+1 per ratio
Response ratio not within above criteria.	-1 per ratio
Response factors correct relative to each other.	+1
Peak area is ≥1,000 counts for FID or ≥10,000 counts for PID, ECD, and NP.	+½ per peak
Peak area is less than that indicated above.	-½ per peak

[a] RT - Retention time.

[b] Counts - Measured in amps/sec; absolute value varies with the detector.

[c] FID - Flame ionization detector.

[d] ECD - Electron capture detector.

[e] PID - Photoionization detector.

[f] NPD - Nitrogen/phosphorus - flame ionization detector.

[g] Points - Points are assigned and added according to the scheme given at the right.

[h] Retention time range optimum.

[i] Indicates a potential positive identification of compound of interest within the sample.

[j] Mandatory criteria - if this criteria is not met, then the points are considered to be zero and are not shown in the above table.

TABLE 48. COMPILATION OF ANALYTICAL RESULTS

	Tenax lab spike				Tenax field blank				Tenax tube 236[e]				Ambersorb tube 272[e]			
		Points				Points				Points				Points		
Compound	FID RT,[a] min	Act.[b]	Pos.[c]	Percent[d]	FID RT, min	Act.	Pos.	Percent	FID RT, min	Act.	Pos.	Percent	FID RT, min	Act.	Pos.	Percent
Acrolein	6.05	3	5	60	5.92	2 1/2	5	50		0	5	0		0	5	0
Acrylonitrile	6.42	2	4	50		0	4	0	6.43	3	4	75		0	4	0
Vinyl acetate		0	5	0	7.41	3	5	60	6.96	5	5	100		0	5	0
Ethylene dichloride	8.08	2	5	0[i]		0	5	0	7.45	2	5	40		0	5	0
Benzene	[j] 7.51	4 1/2	8 1/2	53	7.41	3	5	0[k]	8.05	4	5	80		0	5	0
Carbon tetrachloride						0	5	0	7.97	5	5	100		0	5	0
1,4-Dioxane		0	5	0		0	5	0	8.58	3	5	60		0	5	0
cis-1,3-Dichloropropene	9.56	7 1/2	8 1/2	88		0	8 1/2	0		0	8 1/2	0		0	8 1/2	0
trans-1,3-Dichloropropene	9.80	7 1/2	8 1/2	88		0	8 1/2	0		0	8 1/2	0		0	8 1/2	0
Ethylene dibromide	10.55	4	5	80		0	5	0	10.71	3	5	60	10.59	3	5	60
Tetrachloroethylene	10.99	6 1/2	8 1/2	76	10.86	1/2	8 1/2	6		0	8 1/2	0		0	8 1/2	0
Styrene		0	5	0		0	5	0		0	5	0		0	5	0
Toluene-2,4-diamine		0	8 1/2	0	14.84	2	8 1/2	24		0	8 1/2	0		0	8 1/2	0
Hexachloro-1,3-butadiene	19.82	6 1/2	8 1/2	76		0	8 1/2	0		0	8 1/2	0		0	8 1/2	0
Benzyl chloride	21.23	4 1/2	8 1/2	53	21.19	3 1/2	8 1/2	41	21.06	-1/2	8 1/2	-6		0	8 1/2	0
Di-(2-ethylhexyl) phthalate		0	8 1/2	0	25.74	7 1/2	8 1/2	88		0	8 1/2	0		0	8 1/2	0

(continued)

TABLE 48 (continued)

Compound	Standard mix FID RT, min	Standard mix Points Act.	Standard mix Points Pos.	Standard mix Per-cent	Porapak R tube 220[e] FID RT, min	Porapak R tube 220[e] Points Act.	Porapak R tube 220[e] Points Pos.	Porapak R tube 220[e] Per-cent	Tenax tube 271[f] FID RT, min	Tenax tube 271[f] Points Act.	Tenax tube 271[f] Points Pos.	Tenax tube 271[f] Per-cent	Field samples Average percent Tenax[g]	Field samples Average percent All[h]
Acrolein	6.07	4	5	80		0	5	0	6.16	5	5	100	50	25
Acrylonitrile	6.35	3	4	75		0	5	0	6.41	4	5	80	78	39
Vinyl acetate	6.99	5	5	100	7.27	3	5	60	6.66	3	5	60	80	55
Ethylene dichloride	7.65	4	5	80		0	5	0	7.95	2	5	40	40	20
Benzene	[j]7.93	8 1/2	8 1/2	100[j]	[j]8.13	5 1/2	8 1/2	65	[j]8.18	7 1/2	8 1/2	88	84	58
Carbon tetrachloride[j]													94	63
1,4-Dioxane	8.72	4	5	80	8.66	4	5	80	9.69	3	5	60	60	50
cis-1,3-Dichloropropene	9.32	7 1/2	8 1/2	88	9.24	3 1/2	8 1/2	41	10.39	2 1/2	8 1/2	29	15	18
trans-1,3-Dichloropropene	9.82	7 1/2	8 1/2	88		0	8 1/2	0		0	8 1/2	0	0	0
Ethylene dibromide	10.51	4	5	80	10.66	3	5	60		0	5	0	30	45
Tetrachloroethylene	10.90	5 1/2	8 1/2	65		0	8 1/2	0		0	8 1/2	0	0	0
Styrene	12.74	5	5	100		0	5	0		0	5	0	0	0
Toluene-2,4-diamine		0	8 1/2	0		0	8 1/2	0	NE	NE[l]	NE	NE	NE	0
Hexachloro-1,3-butadiene		0	8 1/2	0		0	8 1/2	0	NE	NE	NE	NE	NE	0
Benzyl chloride		0	8 1/2	0	22.20	3 1/2	8 1/2	41	NE	NE	NE	NE	NE	12
Di-(2-ethylhexyl) phthalate		0	8 1/2	0		0	8 1/2	0	NE	NE	NE	NE	NE	0

[a] Retention time recorded by flame ionization detector response.

[b] Act. - Actual points assigned.

[c] Pos. - Points possible.

[d] Percent = $\frac{\text{Act. points}}{\text{Pos. points}}$ x 100.

[e] Tubes represent a single sample collected by the ambient air collection system.

[f] Replicate sample collected with a portable miniature collection system; analyzed with a slower temperature program.

[g] Mean value of the percent points of the Tenax field samples (tubes 236 and 271).

[h] Mean value of the percent points of all field samples (tubes 236, 272, 220, and 271; or tubes 236, 272, and 220).

[i] Eliminated because benzene/carbon tetrachloride peak had larger percent points and eluted prior to this peak.

[j] Co-eluting peaks.

[k] Eliminated because peak is closer to the retention time of vinyl acetate.

[l] NE - not evaluated.

percentage value does not represent probable certainty, but is merely a score. The lab spike that was analyzed contained ∿3000 ng each of benzene, benzyl chloride, carbon tetrachloride, tetrachloroethylene, ethylene dibromide, hexachloro-1,3-butadiene, and cis-1,3-dichloropropene (some trans-1,3-dichloropropene also was probably introduced as in impurity). It was prepared from a vaporous sample from the Sample Generation System (Appendix B). Note that all of the spike components were potentially identified during the analysis, but acrolein and acrylonitrile were also indicated. The Tenax field blank indicated potential contamination by acrolein, vinyl acetate, tetrachloroethylene, benzyl chloride, and di-(2-ethylhexyl) phthalate; however, some of these compounds [e.g., di-(2-ethylhexyl) phthalate] do not appear in other analyses. Therefore, the blank may have been contaminated in some manner to which the other sorbent tubes were not exposed. The standard mixture (Figure 47) showed potential positive identifications for all of its components when evaluated as previously described (Table 47). Average values were calculated for the percentage scores obtained for the Tenax and all the field samples. Tenax tube #271 was analyzed using a slower temperature-programming rate (3°C/min). It was the first tube of a three-tube series collected in Houston on 30 July 1980 by a portable miniature sampling system (developed under EPA Contract 68-02-2774). Except for the sample volume, it would essentially be a duplicate of the sample collected on Tenax tube #236.

The percentage scores determined in Table 48 were assigned relative qualitative value (i.e., the higher the score the more likely the potential positive identification was correct). These qualitative values are compiled in Table 49 for the Houston field samples. Benzene, carbon tetrachloride, vinyl acetate, dioxane, ethylene dibromide, and acrylonitrile were potentially identified in more than one sample tube. Their identifications range in qualitative value from possibly to probably correct. The chromatograph in Figure 48 presents an expanded view of the ECD trace obtained for Porapak R tube #220. Detector responses (peaks) determined to potentially represent some of the compounds of interest are indicated.

DISCUSSION

As mentioned previously, during the analyses of the Porapak R and Ambersorb tubes the first peaks eluting, after temperature programming was initiated, eluted later than those for the Tenax tube. This was attributed to a possible "solvent effect" created by the large amounts of water in the Porapak R and Ambersorb tubes. Therefore, the water in these tube samples may have displaced early eluting peaks causing retention times to deviate from the retention time ranges of these compounds in the analytical standards. The shifting of compound retention times due to matrix effects represents a major limitation of any $(GC)^2$ analysis. Such matrix effects can be due to any component of a sample

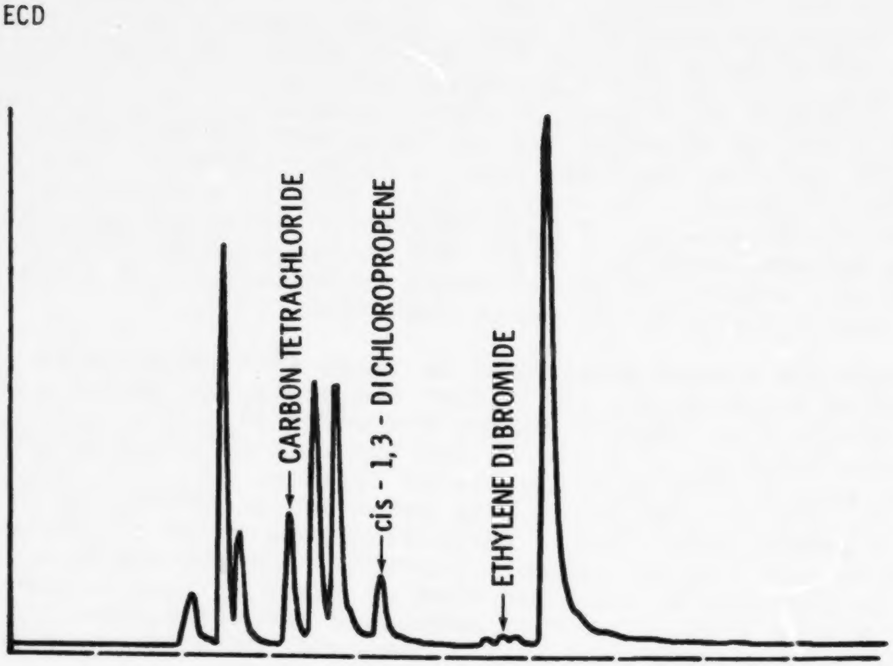

Figure 48. Expanded presentation of Porapak R tube #220, ECD trace.

TABLE 49. RESULTS OF HOUSTON FIELD SAMPLES

Compound	Tenax tube #236[a]			Tenax tube #271[b]			Porapak R[c] tube #220[a]			Ambersorb[c] tube #272[a]			Overall - Houston air			
	Probable[d]	Very possible[e]	Possible[f]	Probable[d]	Very possible[e]	Possible[f]	Probable[d]	Very possible[e]	Possible[f]	Probable[d]	Very possible[e]	Possible[f]	Probable[g]	Very possible[h]	Possible[i]	Slightly possible[j]
Carbon tetrachloride	X			X				X					X			
Benzene		X		X				X						X		
Vinyl acetate	X				X			X						X		
Dioxane		X			X			X						X		
Ethylene dibromide		X						X			X				X	
Acrylonitrile		X			X			X							X	
Acrolein				X												X
Ethylene dichloride			X			X										X
Benzyl chloride									X							X
Dichloropropene									X							X

[a] Tubes represent a single sample collected by the ambient air collection system.

[b] Replicate sample collected with a portable miniature collection system; analyzed with a slower temperature program.

[c] Water in sample may have displaced early eluting peaks causing retention times to deviate from the retention time ranges of these compounds in an analytical standard.

[d] Percent points from Table ≥85.

[e] Percent points from Table = 58 to 84.

[f] Percent points from table = 31 to 58.

[g] Average percent points of all field samples from Table ≥60.

[h] Average percent points of all field samples from Table = 49 to 59.

[i] Average percent points of all field samples from Table = 38 to 48.

[j] Average percent points of all field samples from Table - 1 to 37.

(e.g., water) or the combination of components in that sample. Consequently, compounds can elute within the retention time ranges of other, similar compounds and be mistakenly identified as the other compound. Alternately, compounds actually present in a sample might not be identified at all. All $(GC)^2$ analyses which rely heavily on retention times for compound identification have this limitation. Analyses performed with spectral detection, such as $(GC)^2$/MS or $(GC)^2$/FTIR, use spectra for compound identification and do not rely as heavily on retention times.

In addition to matrix effects, which are a limitation of all $(GC)^2$ analyses, MD$(GC)^2$ has other limitations. The determination of which peaks are simultaneous observed by different detectors is somewhat subjective. Compensation must be made for any offset in the beginning of different detector integrations and allowances made for differences in integration due to different intensities in detector responses. Manual determination of simultaneous peaks allows flexibility of interpretation but is subject to the inconsistency of the interpreter. On the other hand, computer determination allows consistency but not flexibility. Once simultaneous peaks are determined, detector responses and response ratios can be obtained. These results also must be subjectively evaluated to determine whether a compound is potentially identified and the reliability of a potential identification. Compound identification is complicated by co-eluting compounds (e.g., benzene and carbon tetrachloride); by variable detector-response ratios, which occur if one or more detectors are responding in a non-linear response range; and by multiple compounds of similar type having similar detector responses and response ratios eluting within a given retention time range (e.g., cis and trans-1,3-dichloropropene).

The results of the MD$(GC)^2$ analyses of the Houston field samples are summarized in Table 49 and the results of the $(GC)^2$/MS analyses of replicate Houston field samples are summarized in Table 44 (see Section 10). The presence of benzene in the Tenax and Porapak R tubes is indicated in both sets of results. Tetrachloroethylene, which was determined by $(GC)^2$/MS to also be present in the Tenax and Porapak R tubes, was not indicated by the MD$(GC)^2$ analyses. Conversely, carbon tetrachloride, acrylonitrile, vinyl acetate, 1,4-dioxane, and ethylene dibromide were tentatively identified in the field samples by MD$(GC)^2$.

The detectors of the MD$(GC)^2$ system are much more sensitive than is a mass spectrometer, and some of these tentative identifications might be correct but below the detection level of the mass spectrometer. Alternately, some of the discrepancies in compound identification might be due to a combination of the limitations discussed above for MD$(GC)^2$ analyses.

These results indicate that although MD$(GC)^2$ is much more selective and specific than $(GC)^2$ or GC, it cannot replace GC/MS for the unequivocal identification of compounds. MD$(GC)^2$ can be used to indicate the possible presence of selected compounds although matrix effects and other limitations can imply the presence of compounds actually not present and the absence of compounds actually present. Perhaps a better use for MD$(GC)^2$ would be to use this technique to identify various types of compounds in samples and their overall "total" amounts. This would provide much more information than a total chromatographable organics analysis (TCO) about the composition of an air sample, and could perhaps be an indicator of overall air quality in terms of organic pollutants.

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APPENDIX A

METHODS FOR THE SAMPLING AND ANALYSIS OF ORGANIC MATERIALS

SAMPLING

Various sampling methods have been employed to collect organic pollutants for subsequent laboratory analysis. Other methods are available to analyze these pollutants in the field by passing the polluted air or stack gas through analytical equipment as it is collected. This section discusses those methods which can be employed for field use.

Organic pollutants that are present in stack gases, ambient air, and workplace environments exist as particulates, gases, or vapors and therefore require collection techniques specific to those media. Particulates are commonly collected on filters and in cyclones; gases and vapors are either collected in cryogenic traps, polymeric bags, or evacuated cylinders, or trapped in or on various media. Media employed for trapping gases and vapors have included porous polymers, charcoal, silica gel, alumina glass filaments or beads, and organic solvents. The EPA source assessment sampling system (SASS train) has been recently developed to collect stack gas samples which contain particulates and condensed organic vapors adsorbed onto a porous polymer resin. Recommended sample volumes greatly exceed those of conventional stack sampling systems, thus minimizing the problem of sample quantities below the detection limit of analytical equipment. Specific methods of sample collection are discussed in more detail below.

Particulate Collection

Filtering has probably been the most thoroughly investigated of all methods for the collection of atmospheric and stack gas samples. These methods trap particulates and condensed vapors on a filter media. Glass-fiber filters have been most frequently used; however, other filters such as quartz, cellulose, Teflon, and cellulose esters have also been used [50]. Material collected on filters can subsequently be extracted and analyzed for organic components. For ambient air sampling with filters, high-volume sampling systems are needed to collect a sample mass large enough to be above the detection limits of the analytical techniques. High-volume particulate samples have been used in a variety of situations where it was desired to measure organic material in ambient air.

Airborne particulate material has been collected on glass-fiber filters with high-volume air samples mounted aboard ships during cruises of the Mediterranean Sea and Pacific Ocean. These filters were extracted with chloroform, and the lipid components of the extracts were converted to methyl esters for analysis by gas chromatography (GC) [51]. In a survey conducted in Belgium, particulates were collected at 14 sites employing high-volume samplers. The samples were analyzed for total organics and benzo(a)pyrene (BaP). The results showed that high-volume sampling volatilizes a large portion of the organics adsorbed on the particles [52]. Organic materials are also recovered from particulates collected from stack gases. Stack sampling devices collect much lower volumes of gas than do ambient air samplers because of the higher concentration of particles usually occurring in stack gases.

EPA Method 5, illustrated in Figure A-1, is the most widely used stack sampling method for particulate collection [53]. Stack gas is drawn into the system by a vacuum pump through a probe and heated filter and into a set of water impingers. Sampling is conducted isokinetically while traversing the stack to obtain a representative particle size distribution. Another procedure for stack gas particulate collection is EPA Method 17, illustrated in Figure A-2, which is similar to Method 5, except that an in-stack filter is employed [54].

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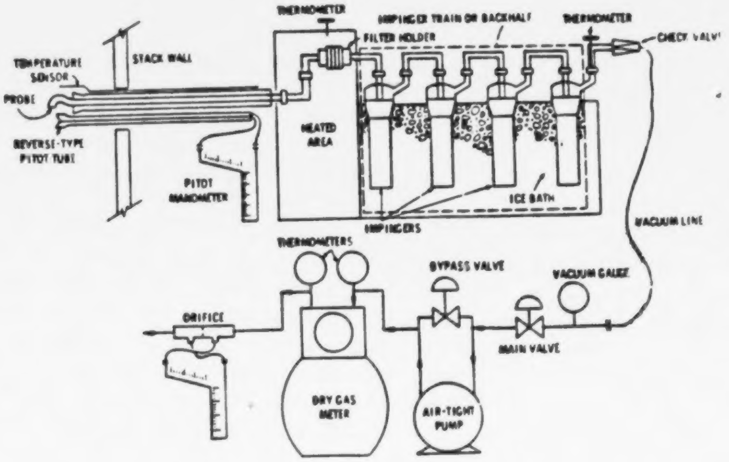
THERMOMETER
IMPINGER TRAIN OR BACKHALF
THERMOMETER
FILTER HOLDER
CHECK VALVE
TEMPERATURE SENSOR
STACK WALL
PROBE
REVERSE-TYPE PITOT TUBE
HEATED AREA
PITOT MANOMETER
ICE BATH
IMPINGERS
VACUUM LINE
THERMOMETERS
BYPASS VALVE
VACUUM GAUGE
ORIFICE
MAIN VALVE
DRY GAS METER
AIR-TIGHT PUMP

Figure A-1. Schematic of EPA Method 5 sampling train for particulates [55].

In-stack filters have been employed to collect particulate samples from coking, smelting, and similar industrial operations. The extracts of these particulates were subsequently analyzed for 14 highly carcinogenic polynuclear aromatic (PNA) compounds [55].

A variety of samplers is available to collect particles of various size ranges. The best known samplers are the Anderson size-fractionating cascade impactors. Particles collected on stages 2 through 7 of an Anderson sampler, representing aerodynamic sizes from 0.43 to 7.0 μm, are purported to be deposited in the pulmonary, tracheobronchial and nasopharyngeal compartments of the respiratory system [50].

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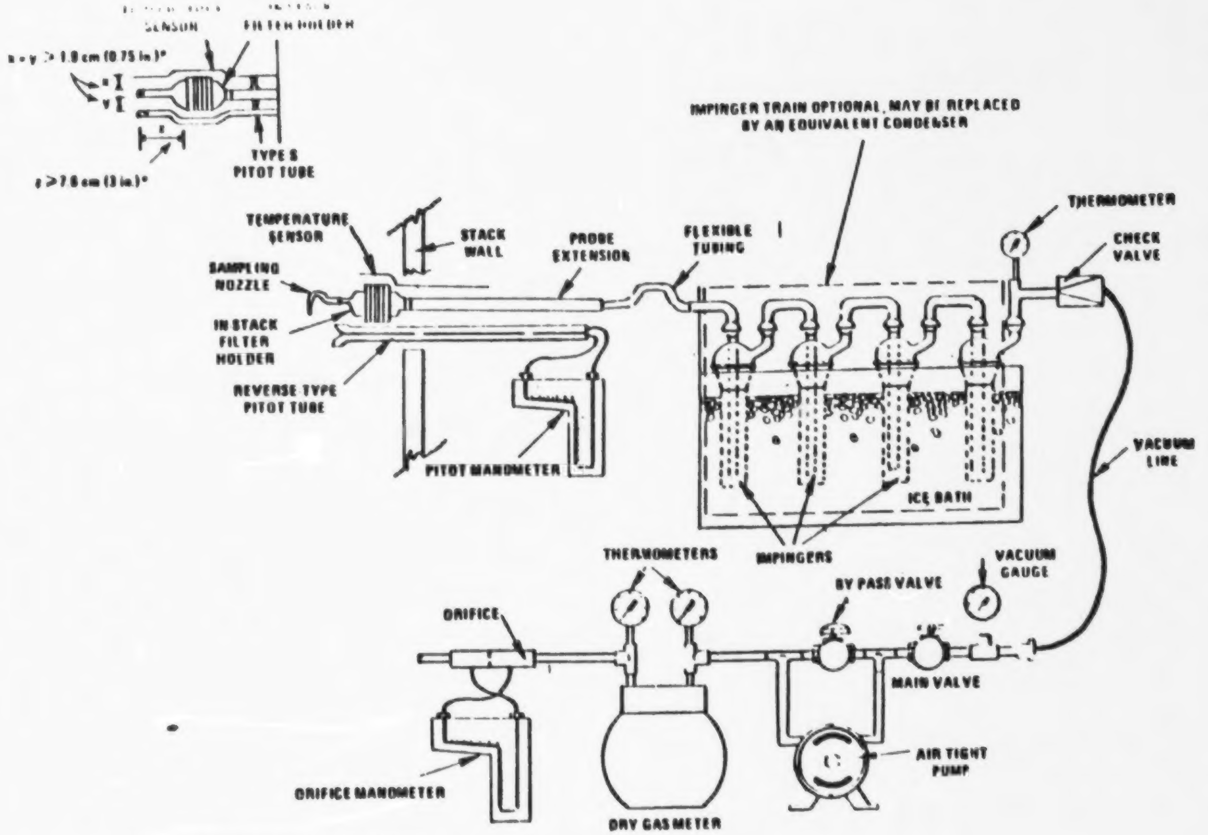
SENSOR
FILTER HOLDER
x + y > 1.9 cm (0.75 in.)*
x
y
z
z > 7.6 cm (3 in.)*
TYPE S PITOT TUBE
TEMPERATURE SENSOR
SAMPLING NOZZLE
IN STACK FILTER HOLDER
REVERSE TYPE PITOT TUBE
STACK WALL
PROBE EXTENSION
PITOT MANOMETER
FLEXIBLE TUBING
IMPINGER TRAIN OPTIONAL, MAY BE REPLACED BY AN EQUIVALENT CONDENSER
THERMOMETER
CHECK VALVE
VACUUM LINE
ICE BATH
IMPINGERS
THERMOMETERS
VACUUM GAUGE
BY PASS VALVE
ORIFICE
MAIN VALVE
AIR TIGHT PUMP
ORIFICE MANOMETER
DRY GAS METER

*SUGGESTED (INTERFERENCE-FREE) SPACINGS

Figure A-2. Particulate-sampling train, equipped with in-stack filter [54].

A comparison of the performance of a membrane-filter personal air sampler with that of a high-volume sampler showed good correlation when suitable care was taken in weighing the membrane filters and in compensating for absorbed water [50].

A similar filtering method has also been employed for collection of organic materials. Mercuric salts and sulfuric acid impregnated filters have been employed in an effort to determine low-molecular-weight mercaptans, dimethyl sulfide, and methylamine in urban and industrial areas. The gases were recovered from the filter, concentrated, and analyzed by GC. This procedure allowed short-term, high-volume sampling to determine the concenration of gases at less than 1 ppb [56]. Glass-fiber filters have also been treated with glycerin tricaprylate and reported to trap tetracyclic arenes with 100% collection efficiency. The method requires the additional step of hydrolyzing the ester before extraction with cyclohexane [50].

A multiparameter fluorescence method for *in-situ* monitoring of stack gas particulates has been reported. The fluorescent emissions from the particulates could be used to characterize the chemical composition of particulates as well as to classify their size. Early measurements of aromatic compounds showed that each sample had a characteristic emission spectra and lifetime. Measurements and discrimination were accomplished using photon counting and fluorescence spectra correlation [57].

An instrument for real-time analysis of airborne particulates has been described in the literature. The average concentration of particulates in the air was determined by impinging the particles on a heated rhenium ribbon and analyzing the ion current with a small, magnetic sector, mass spectrometer. Heavy metals and organic compounds in the particles could be analyzed by this technique [58].

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Extraction of Organic Material from Particulate Samples

Because reliable techniques for the direct analysis of particles for organic compounds are not readily available, the organics associated with collected particulates are often extracted. In many cases organic solvents are employed for extraction, and the resulting solutions are normally concentrated and separated into fractions prior to analysis.

Extraction of polyaromatic hydrocarbons (PAH) from particulates is usually accomplished by a 5- to 12-hour soxhlet extraction with benzene or cyclohexane at the boiling point. The disadvantages of this method are 1) benzene is a human leukemogen, 2) during the extraction and evaporation steps, some of the polar material decomposes and some polymerizes, 3) the extraction time is too long, 4) benzene is a more efficient extractant than cyclohexane but contains much more extraneous polar material in the extract than does cyclohexane, and 5) the reproducibility of the method is not as good as that obtained with some of the more recently developed methods. An independent investigation of the benzene-soluble extraction method pointed out many of its faults and emphasized its poor reproducibility [50].

Airborne particulate matter collected on glass-fiber filters has been extracted with benzene and separated into neutral, acidic and basic fractions. In this study, the acidic fraction was converted to the methylated derivatives before analysis. More than 100 compounds were identified in the acidic fraction consisting mainly of fatty acids and aromatic carboxylic acids. In the neutral fraction, saturated aliphatic hydrocarbons, PAH, and polar oxygenated substances were identified. The basic fraction consisted of nitrogen-containing analogs of the important PAH present in the neutral fraction [59].

In another study particulates collected on glass-fiber filters were soxhlet extracted with cyclohexane, and the organic matter was concentrated and fractionated into chemical classes by adsorption chromatography. The PAH fraction was collected and further fractionated by bond-reverse phase-partition chromatography [60]. Development work in the separation of organic compounds by instant thin layer chromatography (TLC) has also been reported [61]. Soxhlet extraction of filtered airborne particulates with methanol has been employed prior to the analysis of complex organic mixtures [62]. More than 20 aza-arenes and other nitrogen-bases have been identified by employing an isolating technique applied to ambient particulates. An extraction, solvent partitioning, and a sequence of chromatographic separations were employed to identify aza-arenes, quinolines, isoquinolines, and their alkyl derivatives [63].

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Methods other than solvent extraction have also been employed to extract organic material from collected particulate matter. A mechanical disrupting technique capable of extracting the organic content from filtered ambient particulate has been tested and found to compare favorably with the soxhlet extraction method [64]. Hydrofluoric acid has been employed to enrich the PAH content from filtered airborne particulate. The hydrofluoric acid dissolves the glass-fiber filter and collected particles, leaving the organic residue free for solvent extraction. This method is useful for rapid preparation of samples for GC/MS analysis [65].

Soxhlet and ultrasonic extraction procedures were compared for seven different solvents having boiling points ranging from 34°C to 81.4°C. For benzo(a)pyrene and aromatic compounds, the ultrasonic method using methanol as solvent proved to be best. Both methods were applicable for ether, dichloromethane, chloroform, and benzene. The ultrasonic method has the advantages of being rapid, operating at relatively low temperatures (0°C-10°C), and causing no changes in the spectra [50].

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[65] Bove, J. L., and V. P. Kukreja. An Enrichment Method for Polycyclic Aromatic Hydrocarbons Collected on Glass Fiber Filters Using Hydrofluoric Gas. J. Environmental Science & Health - Environmental Science & Engineering, 11(8-9):517, 1976.

Decomposition problems can occur with PAH and polar compounds [50] when solvent desorbed. However, sublimation of PAH from airborne particulate at about 250°C-300°C does not require the use of solvents, can prevent decomposition of compounds when performed under vacuum, can be automated, and can discriminate for low boiling hydrocarbons.

Temperature programming essentially consists of extraction and separation of gaseous pollutants from polymer resins by heating the resin gradually from 0°C to 150°C. This desorbs the material collected, passing it directly to a mass spectrometer for analysis. The disadvantage is artifact formation, the problem of "synthesizing" compounds which were not present originally in the air. Temperature programming cannot separate BaP from benzo(e)pyrene or perylene. TLC cannot separate BaP completely from other PAH. However, with two-dimensional alumina-cellulose acetate TLC, BaP is easily separated from other PAH and the other fluorescent pollutants in organic extracts of airborne particulates [50].

Polytron extraction utilizes a Brinkmann homogenizer which combines the tearing and ripping strength of mechanical energy with the cavitating energy of sonic and ultrasonic sound. The extraction of a large filter (500 cm^2) can be accomplished below room temperature within 5-10 min. Cyclohexane or water work well as the extractant. The disadvantages of this technique are: 1) a pure solvent must be used, and 2) ultrasonic treatment should be kept to a minimum so as to minimize decomposition [50]. A mechanical disruption technique has been employed to extract the organic material from a fiber-glass filter sample. The method compared favorably with soxhlet extraction [64].

Solid Sorbents for Collecting and Concentrating Organic Compounds

Solid sorbent methods for collecting and concentrating organic substances from point source or ambient air employ the adsorption or partitioning properties of the sorbent materials. These materials retain organic substances selectively while passing the major diluent gases like nitrogen and oxygen of air.

The retentive characteristics, varied polarity, and high thermal stability of charcoal, molecular sieves, and porous polymers suggest that these materials might be the best media for efficiently collecting and enriching organic substances although the varied nature of sources requires their evaluation for specific applications.

In selecting a sorbent for high collection efficiency, the recovery of the compound must also be considered. Often a mutal compromise may be necessary to obtain an acceptable system. Table A-1 lists some of the sorbents most used and the types of compounds which could be collected [66].

TABLE A-1. GENERAL SORPTION-DESORPTION SYSTEMS FOR ORGANIC COMPOUNDS

Sorbent	Desorption solvent	Type of compound
Activated carbon	Carbon disulfide, methylene chloride, ethyl ether (1% methanol or 5% isopropanol sometimes added).	Miscellaneous volatile organics: methyl chloride, vinyl chloride and other chlorinated aliphatics, aliphatic and aromatic solvents, acetates, ketones, alcohols, etc.
Silica gel	Methanol, ethanol, diethyl ether, water.	Polar compounds: alcohols, phenols, chlorophenols, chlorobenzenes, aliphatic and aromatic amines, etc.
Activated alumina	Water, diethyl ether, methanol.	Polar compounds: alcohols, glycols, ketones, aldehydes, etc.
Porous polymers	Ether, hexane, carbon disulfide, alcohols.	Wide range of compounds: Phenols, acidic and basic organics, multifunctional organics, etc.
Chemically bonded and other GC packings	Ether, hexane, methanol.	Specialized: high boiling compounds, pesticides, herbicides, polynuclear aromatics, etc.

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[66] Dietrick, M. W., L. M. Chapman, and J. J. Mieure. Sampling for Organic Chemicals in Workplace Atmospheres with Porous Polymer Beads. American Industrial Hygiene Association Journal, 39(5):385-392, 1978.

Polymer Sorbents--

Five groups of porous polymers have been found to be most useful as solid sorbents for collecting the concentrating organic compounds from polluted atmospheres and stack gases; they are: XAD resins, Tenax-GC, the Porapak series, the Chromosorb Century series, and polyimides. These sorbents are finding increased application in stack and ambient air sampling. Several studies have evaluated the effectiveness of sampling with polymer sorbents [67-75]. Polymer sorbent samplers have been shown to

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[67] Adams, J., K. Menzies, and P. Levins. Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds. EPA-600/7-77-044, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1977, 67 pp.

[68] Gallant, R. F., J. W. King, P. L. Levins, J. F. Piecewicz. Characterization of Sorbent Resins for Use in Environmental Sampling. EPA-600/7-78-054, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1978. 163 pp.

[69] Snyder, A. D., F. N. Hodgson, M. A. Kemmer, and J. R. McKendree. Utility of Solid Sorbents for Sampling Organic Emissions from Stationary Sources. EPA-600/2-70-201, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1976, 77 pp.

[70] Rhoades, J. W., and D. E. Johnson. Evaluation of Collection Media for Low Levels of Airborne Pesticides. EPA-600/1-77-050, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1977. 140 pp.

[71] Strup, P. E., P. W. Jones, R. D. Giammar, and T. B. Stanford. Efficient Collection and Analysis of Hazardous Organic Compounds from Combustion Effluents. Battelle-Columbus Laboratory, Ohio. International Conference on Environmental Sensing and Assessment, Las Vegas, Nevada, 14-18 September 1975. Published by IEEE, New York, Vol. 2, Paper 22-3, 1976. 4 pp.

[72] Winterlin, W., D. G. Crosby, and W. W. Kilgore. Analytical Research on Economic and Environmental Toxicants. Grant 67347, U.S. Dept. of Agriculture, Washington, D.C., 1978.

[73] Bunn, W. W., E. R. Deane, D. W. Klein, and A. D. Kleopfer. Sampling and Characterization of Air for Organic Compounds. Water, Air and Soil Pollution, 4(3-4):367-380, 1975.

[74] Barrett, W. J. Identification of Organic Compounds in the Atmosphere. Grant PHS-AP-00454, U.S. Public Health Service, 1968.

[75] Smith, M.S., A. J. Francis, and J. M. Duxbury. Collection and Analysis of Organic Gases from Natural Ecosystems: Application to Poultry Manure. Environmental Science & Technology 11(1):51-55, 1977.

be more efficient than common impinger methods with nearly quantitative recovery for many organic species including polycyclic organic compounds (POM) [71]. Some of the specific applications of polymer sorbents are presented in more detail below.

A study to develop methods for pesticide collection and analysis employed tubes packed with cross-linked polystyrene resin [72]. In a program to sample and characterize ambient air for organic compounds, several polymer resins were employed. Sorption on XAD-2 resin followed by solvent elution, and sorption on Tenax-GC followed by direct desorption onto a GC column identified 82 compounds including large quantities of phenol and phenol-formaldehyde resin intermediates [73]. In another study a 0.15-m long, 3.2-mm diameter copper tube was filled with an ordinary GC column packing for concentrating traces of oxygenated organic compounds in air. Samples of approximately one liter were drawn through the tube using a rubber aspirator bulb [74]. Porapak QS-Carbosieve B traps were used to identify volatile compounds generated from chicken manure. Various alcohols, ketones, esters, and carboxylic acids together with dimethyl sulfide were detected [75].

Tenax-GC cartridges have been used to collect organic vapors from the ambient air of three major cities. Vapors were thermally desorbed and analyzed by a capillary GC/MS technique. Twenty-one halogenated hydrocarbons were detected, including vinyl chloride and trichloroethylene [76]. Epoxides such as ethylene oxide, propylene oxide, and styrene oxide have been tentatively identified in air samples collected on Tenax-GC as well as dimethylnitrosamine [50]. Tenax-GC has been suggested as the best available sorbent for general use. It has been thoroughly studied in the laboratory and in the field and has been applied to the sampling of carcinogenic vapors in the atmosphere. It has a high operating temperature in that even up to 350°C little background bleeding is observed. The effects of transportation and storage of bis(chloromethyl) ether on Tenax-GC have been investigated. Immediate analysis gave 100% recovery; following transportation of a cartridge from Research Triangle Park, N.C., to San Francisco, CA and back (total transportation time of 6 days), the recovery dropped to 58 ± 5% after 1 week and 41 ± 4% after 2 weeks. Without transportation the recovery was 65 ± 5% in 1 week [50].

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[76] Pellizzari, E. D., J. E. Bunch, R. E. Berkley, and J. McRae. Determination of Trace Hazardous Organic Vapor Pollutants in Ambient Atmospheres by Gas Chromatography/Mass Spectrometry/Computer. Analytical Chemistry, 48(6):803, 1976.

A method to sample for environmental contamination of polychlorinated naphthalenes (PCN) was developed and consisted of a glass-fiber filter and two precleaned polyurethane foam plugs in tandem. Recovery of PCN from the foam and filter was accomplished by triple extraction with toluene [77]. Polyurethane foam, known for its capacity to remove PCB's from sea water, is finding increased potential for removing PCB's from air samples. Several studies report polyurethane foam being used to sample ambient air in high-volume samplers for collection of PCB's and chlorinated pesticides. Removal of the collected organics from the foam is normally accomplished by organic solvent extraction [78-80].

PCB emissions have been measured from stacks of municipal waste, industrial waste, and sewage sludge incinerators and from capacitor and transformer filling plants. Collection was accomplished by water impingement and adsorption on Florisil or direct adsorption on Florisil. Samples were extracted with hexane and concentrated through evaporation of the solvent [81]. Chromosorb 101 has been used to efficiently trap vapors of hexachlorobenzene

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[77] Erickson, M.D., R. A. Zweidinger, L. C. Michael, and E. D. Pellizari. Environmental Monitoring Near Industrial Sites: Polychloronaphthalenes. EPA-560/6-77-019, U.S. Environmental Protection Agency, Washington, D.C., June 1977. 267 pp.

[78] Lewis, R. G., A. R. Brown, and M. D. Jackson. Evaluation of Polyurethane Foam for Sampling of Pesticides, Polychlorinated Biphenyls and Polychlorinated Naphthalenes in Ambient Air. Analytical Chemistry, 49(12):1668-1672, 1977.

[79] Margeson, J. H. Methodology for Measurement of Polychlorinated Biphenyls in Ambient Air and Stationary Sources - A Review. EPA-600/4-77-021, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1977. 39. pp.

[80] Bidleman, T. F., and C. E. Olney. High-Volume Collection of Atmospheric Polychlorinated Biphenyls. Bulletin of Environmental Contamination and Toxicology, 11(5):442-449, 1974.

[81] Haile, C. L., and E. Baladi. Methods for Determining the Polychlorinated Biphenyl Emissions from Incineration and Capacitor and Transformer Filling Plants. EPA-600/4-77-048, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977. 94 pp.

(HCB) and hexachloro-1,3-butadiene (HCBD) from air at a sampling rate of 3 L/min decreased the efficiency by 20% [82].

Other Sorbent Collection Materials--

Activated charcoal has found widespread usage for sampling organics especially in the collection of solvent vapors. A charcoal-tube sampling procedure was tested on vapors of benzene, carbon tetrachloride, chloroform, dioxane, ethylene dichloride, trichloroethylene, meta-xylene, and two solvent mixtures for NIOSH methods development [83]. A later study reports the development by NIOSH of a personnel atmospheric sampler consisting of a glass tube containing layers of activated charcoal, urethane foam, and glass wool for organic pollutant sampling. Organics trapped on the charcoal are removed with carbon disulfide [84]. Activated carbon was also used to sample emissions from grain fermentation units in a whiskey distillery. Ethyl acetate, ethyl alcohol, n-propyl alcohol, isobutyl alcohol, isoamyl alcohol, and isoamyl acetate were adsorbed on the carbon and identified by GC [85]. Vinyl chloride monomer (VCM) was quantified using charcoal cartridges to sample automobile interior atmospheres. Qualitative sampling with Tenax-GC identified 147 organic compounds in the automobiles not present in the surrounding air [86]. Dimethyl nitrosamine was also reported to be collected by activated charcoal [50].

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[82] Mann, J. B., H. F. Enos, J. Gonzalez, and J. F. Thompson. Development of Sampling and Analytical Procedure for Determining Hexachlorobenzene and Hexachloro-1,3-butadiene in Air. Environmental Science & Technology, 8(6):584, 1974.

[83] Reckner, L. R. and J. Sachdev. Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents. NIOSH-75/184, National Institute for Occupational Safety and Health, Cincinnati, Ohio, June 1975, 229 pp.

[84] Flisak, F., and J. Kubarewicz. Sampling Methods and Instrumental Analyses of Airborne Toxic Chemicals in Workroom Environments. In: Proceedings of a Special Conference on Industrial Pollution Control Measurement and Instrumentation, Technamic Publishing Co., Westport, Connecticut, 1976, pp 162-165.

[85] Carter, R. V. and B. Linsky. Gaseous Emissions from Whiskey Fermentation Units. Atmospheric Environment, 8(1):57-62, 1974.

[86] Zweidinger, R. A. Organic Emissions from Automobile Interiors. EPA-600/7-77-149, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1977. 90 pp.

Other sorbent materials reported include silica gel, alumina, and glass plates. Sulfuric acid-coated silica gel was found to be effective in the collection of low-boiling aliphatic amines, low-boiling hydrazines, pyridines, and formaldehyde. Solvent elution was used to remove the sample from the silica gel. Alumina was also studied for sampling formaldehyde vapors [87]. The glass plate sampling technique has been shown to be a simple method for sampling organic films that accumulate on items exposed to a tropical environment. The glass plate can be placed adjacent to a test item stored in the tropics and the effects of environmental chemicals studied without destroying the test item [88].

Desorption of Solid Sorbents--
After sample collection, tubes containing the solid sorbent and adsorbed organic chemicals are returned to the laboratory and the organic chemical is recovered, most frequently by solvent desorption. Many solvent desorption techniques are identical to those described for extraction of organic material from particulate samples.

Porous-polymer-bead sorbents offer the option of thermal desorption for sample recovery. The trapped materials are thermally desorbed from the collection column and directly transferred to the GC analytical column within the gas chromatograph oven. This technique is used frequently in air pollution studies and is equally applicable for industrial hygiene applications. The thermal desorption process has several advantages over solvent desorption procedures. High sensitivity is possible with thermal desorption because the entire collected sample can be analyzed at one time. Also, no solvents are present which not only reduce sensitivity but obscure chromatographic regions and may present potential health hazards.

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[87] Distenfeld, C. H., and J. R. Klemish. High Efficiency Mixed Species Radioiodine Air Sampling Readout, and Dose Assessment System. Presented at IAEA/OECD Handling of Radiation Accidents, Symposium, Vienna, 28 February - 4 March 1977, p 463.

[88] Sprouse, J. F. New Sampling Technique for Identifying Organic Film Accukulation on Army Material in the Tropics. Presented at 6th Annual Symposium on Environmental Research, Edgewood Arsenal, Aberdeen Proving Ground, Maryland, 29 April - 1 May 1975. Published by Dept. of Army, Edgewood Arsenal, Aberdeen Proving Ground, Maryland, EO-SP-76001, 1976.

Commercial instrumentation for thermal desorption is now available from several sources. These units are designed primarily for the analysis of volatile materials such as process solvents. They are less applicable for high boiling chemicals and those sensitive to metal surfaces. A simple method has been developed to modify a laboratory gas chromatograph for thermal desorption studies, including those of high boiling and sensitive materials. A three-way valve is utilized which allows ready return of the gas chromatograph to the conventional operating mode. A modification is also described which will permit splitting of the collected sample so that a portion may be preserved for a second analysis [89].

Solid Sorbent Sampling Systems--
A very simple sampling system using the porous polymer approach is shown in Figure A-3. This system, suitable for higher molecular weight hydrocarbons, consists of a 6.3 mm or 9.5 mm stainless-steel tube, 0.15 m long, packed with porous polymer bead material. This sampling tube is attached to a pump and a gas meter [89]. The pump is required because there is an appreciable pressure drop due to the packing in the tube.

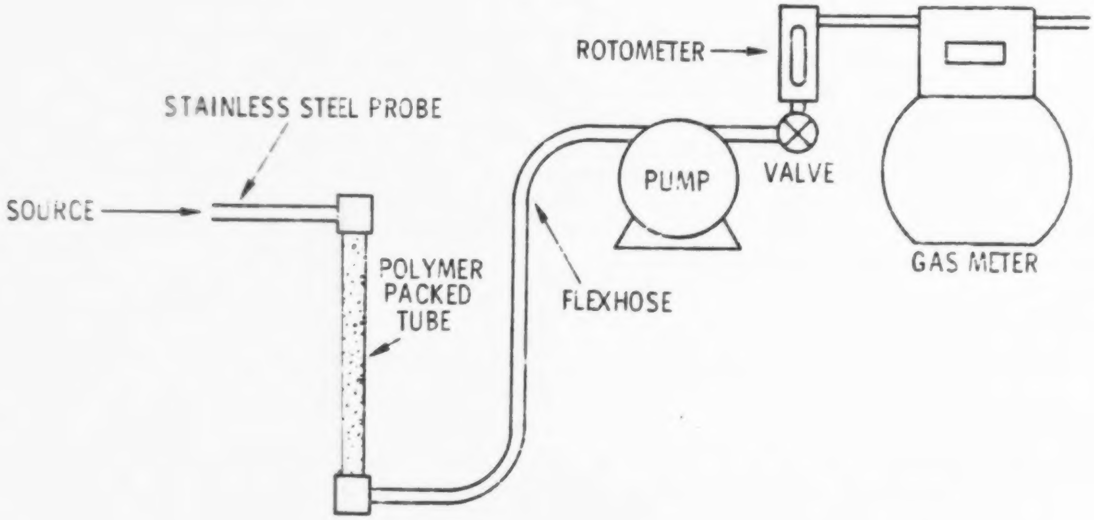

Figure A-3. Porous polymer vapor sampling method [40].

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[89] Feairheller, W. R., P. J. Marn, D. H. Harris, and D. L. Harris. Technical Manual for Process Sampling Strategies for Organic Materials. EPA-600/2-76-122, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1976.

In a similar train, shown in Figure A-4, the pump is replaced with an evacuated cylinder to eliminate pump fluctuations in the sample lines [89]. The cylinder is equipped with a thermocouple or other temperature readout and a vacuum guage. A glass sampling bulb is used to back up the polymer-packed tube to permit at least qualitative identification of low-molecular-weight gaseous species. Typical flow rates of 100-200 mL/min for 20 minutes will provide two to four liters of sampled gas. The temperature and pressure differential in the cylinder before and after collection provides the necessary volume of gas sampled. Some of the organic materials detected by this procedure from a point system and polymer curing ovens are listed in Table A-2 [89].

A more complex system for sampling organic pollutants in stack gases is the EPA source assessment sampling system (SASS train) [90]. This system was developed to efficiently collect at a detectable level all nonvolatile organic compounds present in a flue gas stream including those that exist as a solid, liquid, or vapor. In addition, this system is useful for collecting volatile materials, thus yielding a complete evaluation of the emission source. This provision adds a great deal of complexity to the sampling system. In order to provide the entire range of capability, this system combines a triple cyclone approach for size fractionation of particulate, an organic adsorber employing a polymer sorbent, and an inorganic trace element impinger system. A schematic diagram of the sampling system is shown in Figure A-5 [90]. A major feature of the SASS train is that it samples inorganic and organic emissions simultaneously. Inorganic species are primarily collected by the cyclones and filters. Volatile inorganics are collected in the solid sorbent trap and impinger solutions. Organic species are primarily collected in the solid sorbent trap, although other portions of the train (particulate samples, impinger solutions, rinse solutions) are solvent extracted to recover any other organic material.

Other Means of Entrapment of Organic Pollutants

Probably the most basic technique for collecting air samples for analysis of organic pollutants is the use of evacuated bags or cylinders. Samples are drawn into these containers and transported to a laboratory for analysis of the collected gas either directly or after a concentration step. Commonly used bags are made of Scotchpac, Tedlar and Teflon. Solvent traps have also been used to collect organic compounds. In one study ethylene

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(90) Hamersma, J. W., S. L. Reynolds, and R. F. Maddalone. IERL-Procedure Manual: Level I Environmental Assessment. EPA-600/2-76-160a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1976. 147 pp.

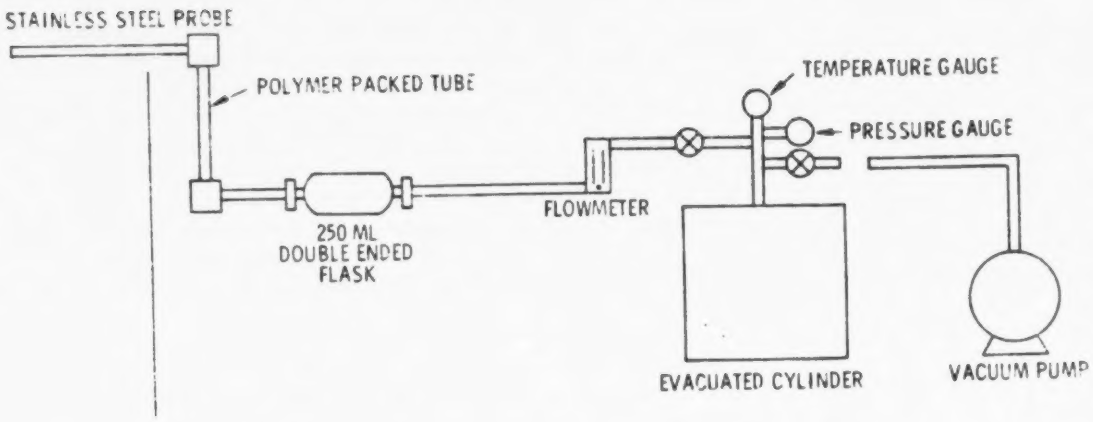
STAINLESS STEEL PROBE
POLYMER PACKED TUBE
250 ML
DOUBLE ENDED
FLASK
FLOWMETER
TEMPERATURE GAUGE
PRESSURE GAUGE
EVACUATED CYLINDER
VACUUM PUMP

Figure A-4. Alternate porous polymer system for organic vapors [89].

TABLE A-2. ORGANIC SUBSTANCES COLLECTED FROM PAINT AND POLYMER CURING OVENS BY POROUS POLYMER ADSORPTION AND ANALYZED USING GC/MS [89].

Methanol
Ethanol
Isopropanol
2-Ethoxyethanol
Isobutanol
n-Butanol
C_5 Alcohols
n-Propanol
2-Methybutanol
Ethylene glycol/monoethyl ether
2-(2-Ethoxyethoxy)ethanol
Formaldehyde
Acetaldehyde
Acrolein
Acetone
Methyl ethyl ketone
Diethyl ether
Butyl acetate
Saturated hydrocarbons

2-Ethoxyethylacetate
Chloroform
Methylene chloride
Cyclohexane
Dimethylcyclohexane
Benzene
Toluene
Xylenes
Styrene
Methylstyrene
Dimethylstyrene
C_3 Alkylbenzenes
C_4 Alkylbenzenes
C_4 Substituted styrene
Trichloroethane
Dichloroethylene
Carbon disulfide
Isopropylbenzene
Phenol
Benzaldehyde

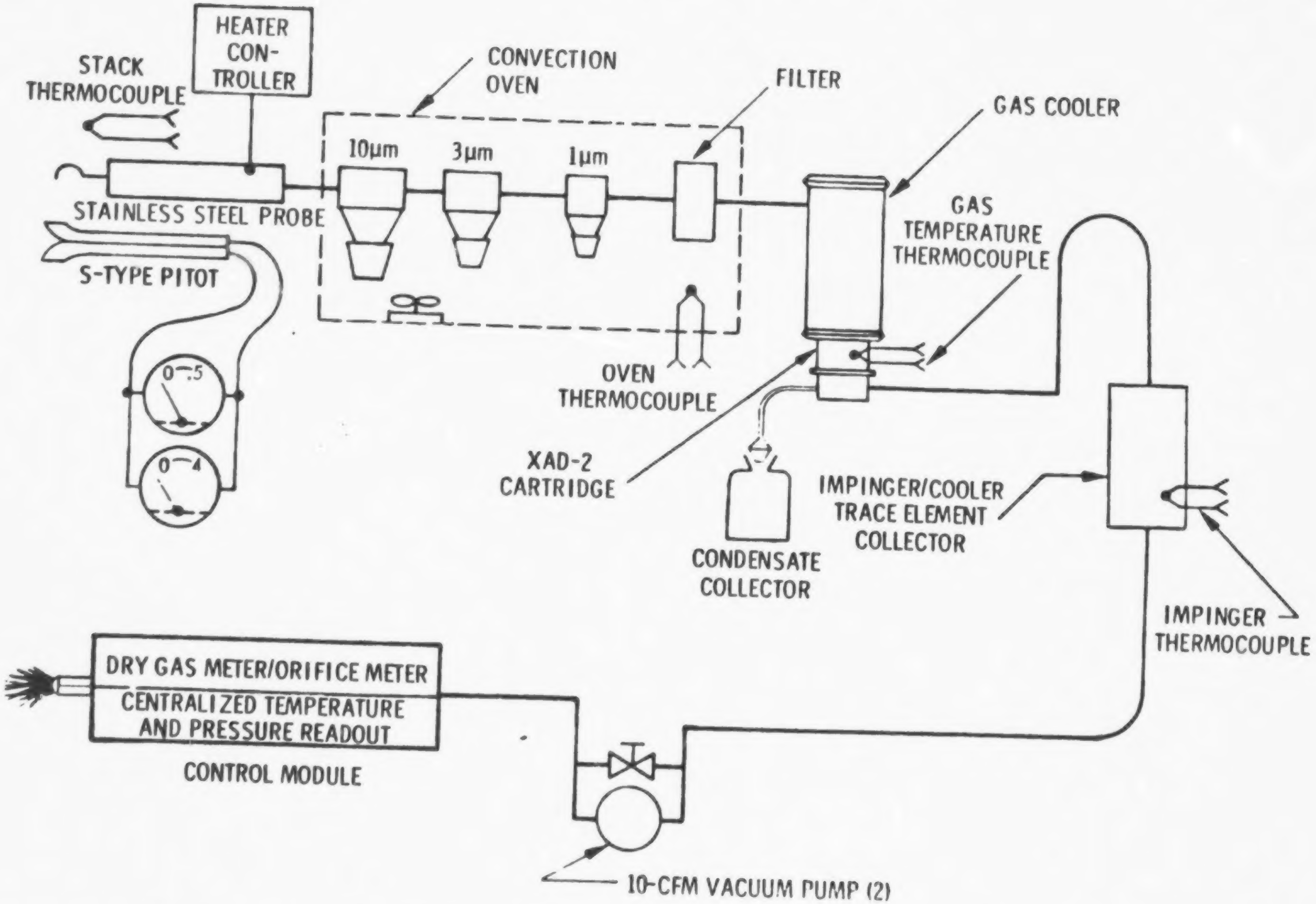
STACK THERMOCOUPLE
HEATER CON-TROLLER
CONVECTION OVEN
FILTER
GAS COOLER
10µm
3µm
1µm
STAINLESS STEEL PROBE
S-TYPE PITOT
GAS TEMPERATURE THERMOCOUPLE
0–.5
0–4
OVEN THERMOCOUPLE
XAD-2 CARTRIDGE
CONDENSATE COLLECTOR
IMPINGER/COOLER TRACE ELEMENT COLLECTOR
IMPINGER THERMOCOUPLE
DRY GAS METER/ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10-CFM VACUUM PUMP (2)

Figure A-5. Schematic of source assessment sampling system [90].

glycol was the trapping solvent for pesticides in the environment. The trapping solvent was extracted with methylene chloride followed by fractionation and cleanup by elution through a silica gel column [91].

Cryogenic sampling has also been employed as a means of concentrating trace organic compounds for chemical analysis. A three-stage cryogenic sampler commonly employs a series of condensers at 0°C (ice water), -78°C (dry ice), and -175°C (liquid nitrogen). Liquid oxygen formation in the third stage is prevented by using a gaseous nitrogen flush [92]. Total organic carbon has been determined on samples from a system employing a dry-ice trap followed by an evacuated 8-liter tank [93]. A dry-ice cold trap has been reportedly used to collect dimethyl-nitrosamine followed by methylene chloride extraction [50].

An alternative method of sampling (wherein chloromethyl methyl ether and bis(chloromethyl) ether can be collected) consists of collection in glass impingers containing a methanolic solution of the sodium salt of 2,4,6-trichlorophenol. Reaction of the chloromethyl ethers with phenol forms stable derivatives with significantly increased detector sensitivity; the chloromethyl methyl ether and the bis(chloromethyl) ether are detected at the 3.3 $\mu g/m^3$ and 4.7 $\mu g/m^3$ levels, respectively. Two impingers must be used in series to trap the compounds in approximately 90% yield [50].

SEPARATION AND ANALYSIS

Samples collected from ambient air and stack gases for organic material analysis will be in the form of particulate, condensed vapors, materials trapped in solution or adsorbed onto solids, or gases. Gases and some liquid samples may be analyzed directly, but particulates, solid sorbents, and other liquid samples need to be extracted and put into solution. Methods for extraction have been discussed in the previous section. Because of the complexity of most samples, a separation step must be employed prior to analyses. This step separates a sample into fractions thus reducing potential ambiguities in the determination of organic components.

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[91] Kutz, F. W., and H. S. C. Yang. A Note on Polychlorinated Biphenyls in Air. U.S. Environmental Protection Agency, Washington, D.C. (PB-275 978).

[92] Conkle, J. P., and R. L. Miller. Cryogenic Sampling of Ambient Atmospheres as a Means of Concentrating Trace Organic Compounds for Chemical Analyses. Presented at the 6th Annual Symposium on Environmental Research, Edgewood Arsenal, Aberdeen Proving Ground, Maryland, 29 April - 1 May 1975. Published by Dept. of Army, Edgewood Arsenal, Aberdeen Proving Ground, Maryland, EO-SP-76001, 1976.

[93] Salo, A. E., W. L. Oaks, and R. D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. J. Air Pollution Control Association, 25(4):390-393, 1976.

Sample analysis can be carried out by a number of techniques which can be grouped into the general categories of 1) chromatographic methods, 2) mass spectrometry, 3) visible and near-visible spectrum measurement, 4) electrochemical techniques, and 5) other methods. These analytical techniques along with methods of separation are discussed in this section.

Sample Separation

Techniques for separating a liquid sample into various fractions for analysis usually rely on the difference in physical properties between organic components. A technique has been used which separates the organic extract of a particulate sample into fractions by means of successive solvent extractions. Primary organics were estimated from the carbon solubilized in cyclohexane, and secondary organics were estimated from the carbon solubilized in successive extraction with benzene and methanol-chloroform. An upper limit estimate of the elemental carbon was obtained from the carbon that remained insoluble [94].

In another study, airborne particulates were collected and extracted with benzene. The extract was then separated into neutral, acidic, and basic substances. The acid fraction was converted to methylated derivatives and found to consist of a homologue series of fatty acids and aromatic carboxylic acids. The neutral fraction consisted of saturated aliphatic hydrocarbons, PAH, and polar oxygenated substances. The basic fraction consisted of nitrogen-containing analogs of the important polyaromatic hydrocarbons present in the neutral fraction [59].

In a study of the nonvolatile fatty acids in cigarette smoke, particulate matter underwent a serial extraction, methyl ester formation, Florisil column cleanup, and analysis by GC. Fatty acids in the 16-18°C range were determined in tobacco smoke by this technique [95].

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[94] Appel, B. R., P. Colodny, and J. J. Wesolowski. Analysis of Carbonaceous Materials in Southern California Atmosphere Aerosols. Environmental Science & Technology, 10(4):359-363, 1976.

[95] Guerin, O. G., and W. T. Rainey. Gas Chromatographic Determination of Nonvolatile Fatty Acids in Cigarette Smoke. Analytical Chemistry, 46(6):761-763, 1974.

The most widely used methods of separation probably employ some type of chromatography. Chromatographic separation has been performed on various media. Silica gel columns have been used in the chromatographic fractionation and cleanup of sample extracts containing chlorinated pesticides, polychloronaphthalenes, and PAH compounds [77, 96, 97].

A method has been described utilizing paper chromatography and consisting of column chromatographic cleanup and separation of B(a)P from the other PAH on acelylated paper. After evaporation, the B(a)P spot is dissolved in sulfuric acid and analyzed by a fluorimetric technique [50]. A similar separation technique, thin layer chromatography (TLC), was coupled with a spectrophotofluorometric procedure and used for the rapid determination of 7,8-benz[de]anthracen-7-one and phenalen-1-one in organic extracts of airborne particulates [61]. Because of the complex nature of combustion emissions, liquid chromatography has been employed to initially separate the collected species into chemical classes after extraction from polymer sorbent collection media [71].

An unambiguous identification of more than 20 aza-arenes and other nitrogen-bases previously unidentified in ambient particulates was accomplished through isolation of the compounds of interest. After extraction from the particulate matter, the organic sample was separated using solvent partitioning and a sequence of chromatographic separations [63].

Manual column chromatography has been extensively used for the separation of B(a)P and other PAH obtained from air samples. B(a)P is usually separated out with benzo(e)pyrene, perylene, benzo(b)fluoranthene and benzo(k)fluoranthene. With poor separation this mixture can even contain benzo(ghi)perylene and anthracene. With a long enough column B(a)P can be separated from the benzofluoranthenes. Unfortunately this type of separation can take half a day. The fairly good resolution of a longer column is tempered with the longer times necessary for separation and for a spectral examination [50].

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[96] Akin, F. J., M. E. Snook, R. E. Severson, W. J. Chamberlain, and D. B. Walters. Identification of Polynuclear Aromatic Hydrocarbons in Cigarette Smoke and Their Importance as Tumorigens. J. National Cancer Institute, 57(1):191-195, 1976.

[97] Sherma, J., and T. M. Shafik. A Multiclass, Multiresidue Analytical Method for Determining Pesticide Residues in Air. Archives of Environmental Contamination and Toxicology, 3(1):55-71, 1975.

High performance liquid chromatography (HPLC) has the potential to separate B(a)P from other PAH within minutes. Using a 40% cellulose acetate column, B(a)P was readily separated from other PAH by HPLC. With columns of Durapak OPN and cellulose acetate, a much larger number of PAH were resolved. The excitation and emission spectra of PAH separated by HPLC could be recorded during the separation by stopping the elution at peak maxima. The main problems of cellulose acetate separation in HPLC is that 1) cellulose acetate packs down during separation and stops the flow, and 2) cellulose acetate washes off the column [50].

Very good resolution for the separation of B(a)P and B(e)P using sodium chloride-Chromosorb columns has been reported. However, other workers attempting to reproduce these results have had difficulties. Excellent separation of B(a)P from B(e)P has been obtained with a nematic liquid crystal column, but the column bleeds so badly at the recommended elevated temperature that the resolution disappears after a few runs [50].

An HPLC method has been developed for class fractionation of the organic material extracted from atmospheric particulate samples. The PAH fraction was collected and further fractionated using bonded reverse phase partition chromatography [60]. Chromatographic separation techniques are often coupled directly to a detector or other means of measurement and identification; applications of these methods are discussed later in this section.

Depending on the analytical technique employed, the separate sample fractions may need to undergo a volume reduction or be dried and redissolved. Drying at elevated temperatures is not possible because of potential evaporation or degradation of organic components. The Kuderna-Danish apparatus has been used for reducing the volume of organic sample fractions after chromatographic separation [77]. A small, easily assembled, freeze-drying unit was used to dry a number of samples of various sizes simultaneously. Evaporation from the frozen or cooled sample surface reduced the danger of damaging sensitive organic components [98].

Analytical Techniques

Various techniques exist for determining the identity and quantity of organic pollutants. Many methods are useful for screening or semiquantitative and qualitative determinations.

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[98] Wittgenstein, E., E. Sawicki, and R. L. Antonelli. Freeze-Drying in the Recovery of Organic Material from Extracts of Air Particulate Matter. Atmospheric Environment, 5(9):801-810, 1971.

These methods usually rely on inference techniques for identification of organic components rather than on direct identification. Mass spectrometry and electron capture detectors are used for quantitative identification of organic components. The use of several techniques in tandem (multi-instrument approach) can result in reduced ambiguity and improved sensitivity.

Gas Chromatographic Techniques--
Gas chromatography, coupled with one of several detectors, has been frequently applied in the measurement of organic pollutants. A gas chromatograph with a flame ionization detector (GC/FID) was used in the analysis of PCB emissions from various industrial sources. Sample preparation included extraction with hexane and perchlorination. PCB content was measured as the de-chlorinated isomer [81]. In another study, atmospheric organic pollutants were concentrated on GC packing material in the field. Analysis consisted of thermally desorbing the organic material directly into a GC/FID or a GC with a flame photometric detector (GC/FPD). Quantitative recovery and part-per-billion (ppb) sensitivity have been reported using this technique [99].

Many studies report the use of gas chromatography without specifying the detection technique. One such study reports the use of GC to determine ppb concentrations of sulfur- and nitrogen-bearing organic gases [56]. Pyridine and 2-aminopyridine were identified by using a GC technique developed to analyze vapors collected on a solid sorbent [87]. Gas chromatography was empolyed to obtain quantitative and qualitative information on the methanol extract of airborne particulate samples [62]. Samples of air pollutants from grain fermentation units were analyzed using GC. Identified in the sample were ethyl acetate, ethyl alcohol, n-propyl alcohol, isobutyl alcohol, isoamyl alcohol, and isoamyl acetate [85]. In other studies, GC has been used for the analysis of organochlorine and organophosphate pesticides, PCB's, polychlorinated naphthalenes [78], benzene, carbon tetrachloride, chloroform, dioxane, ethylene dichloride, trichloroethylene, meta-xylene [83], fatty components of airborne particulate matter containing 12 to 18 carbon atoms in length [51], and benzo(a)pyrene [52]. An automatic continous GC has been used to monitor bis(chloromethyl) ether in air samples at less than ppb levels. The monitor utilizes solid sorbents for gas-phase enrichment, thermal elution, and two GC columns [100].

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[99] Russel, J. W. Analysis of Air Pollutants Using Sampling Tubes and Gas Chromatography. Environmental Science & Technology, 9(13):1175-1178, 1975.

[100] Frankel, L. S. and R. F. Black. Automatic Gas Chromatographic Monitor for the Determination of Parts-Per-Billion Levels of Bis(Chloromethyl) Ether. Analytical Chemistry, 48(4):732-737, 1976.

A system employing GC and catalytic combustion has been reported which yields the total organic carbon content of a sample collected from a stack or vent in a freeze-out trap [93]. A pyrolysis-GC system provided with a data handling unit has been employed in the separation and identification of organic materials. The system separates a sample mixture into components and then pyrolyzes these components one at a time. The pyrolysis products are separated by two chromatographic systems and, from their identity, the original material can be identified [101]. This same system, when coupled with a mass spectrometer, has been used to analyze more than 175 organic molecules comprising the insoluble carbonaceous components of atmospheric particulate matter extract [102].

A GC/atomic absorption apparatus has been constructed for the measurement of toxic volatile organometallic species released from aquatic sediments [103]. A gas chromatographic on-column concentrating technique has been developed for the analysis of halocarbons in atmospheric gas mixtures, thus eliminating the use of cold traps. A coulometric detector is employed which is specific for the quantitative analysis of chlorinated, brominated, or iodated hydrocarbons [104].

Electron Capture Gas Chromatography--
Electron capture gas chromatographic (EC/GC) analysis schemes have been reported for effective quantification of low-molecular weight halocarbons [105]. Ambient air levels of methylchloroform

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[101] Feairheller, W. R., M. D. Schumacher, and W. D. Ross. Research on the Thermolytic Dissociation of Molecules. AFML-TR-74-83, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio, May 1974. 67 pp.

[102] Kunen, S. M., K. J. Voorhees, C. A. Hill, F. D. Hileman, and D. N. Osborne. Chemical Analysis of the Insoluble Carbonaceous Components of Atmospheric Particulates with Pyrolysis/Gas Chromatograph/Mass Spectrometry Techniques. In: Proceedings of the 70th Annual Meeting, Air Pollution Control Association, Toronto, Ontario, 20-24 June 1977. Published by Air Pollution Control Association, Pittsburgh, Pennsylvania, 1977. Paper 77-36.

[103] Jewett, K. L., and G. E. Parris. Environmental Chemistry. Contract 3130117. National Bureau of Standards, Washington, D.C. 1977.

[104] Williams, F. W., M. E. Urnstead, and J. E. Johnson. Determination of Trace Quantities of Halogenated Hydrocarbons in Gas Samples. NRL-6964, Naval Research Laboratory, Washington, D.C., 6 November 1969. 18 pp.

[105] Su, Shih-Wu. Low Molecular Weight Halocarbons. NSF/IDOE-77-36, National Science Foundation, Washington, D.C., 1976. 15 pp.

and trichloroethylene have been determined on site by direct injection of ambient air into a GC followed by detection and quantification with an electron capture detector [106, 107]. The most promising method of analyzing source and ambient air samples for PCB's is reported to be analysis by electron capture gas chromatography. Quantitation is achieved by perchlorination of PCB's to decachlorobiphenyl [79]. Bis(chloromethy) ether (BCME) and chloromethyl methyl ether (CMME) have been quantified using electron capture/GC. The method involved the collection of air samples in a methanolic solution of the sodium salt of 2,4,6-trichlorophenol thus forming stable derivatives with BCME and CMME [50]. Electron capture-GC has also been used to determine chlorinated pesticide residue in air. Prior to analysis, samples were collected in ethylene glycol traps, extracted with methylene chloride, and fractionated in a silica gel column [97].

Mass Spectrometry--

Mass spectrometry is another technique that has been used lately. It has been interfaced with temperature programming, thin-layer chromatography, and gas chromatogrphy for the analysis of organic pollutants. The problem with temperature programming as a separation step is that isomers and other compounds with closely similar sublimation or boiling points would not be separated; for example, compounds like B(a)P and B(e)P would not be separated. In addition, there would be possibilities of decomposition and artifact formation [50].

Gas chromatography-mass spectrometry (GC-MS) with computerized data acquisition has been applied to the analysis of the extract from airborne particulates. Acidic, basic, and neutral fractions of the extract were analyzed. The generation of mass chromatograms for specific ion-fragment masses permitted the location of mass spectra. Comparison with reference data led to identification of more than 100 compounds including aliphatic hydrocarbons, PAH, polar-oxygenated substances, fatty acids, carboxylic acids, and nitrogen-containing analogs of the important PAH compounds present [59]. Analysis by GC-MS of the ether extract of automobile exhaust fine particulates showed the presence of hundreds of compounds including about 50% saturated aliphatics,

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[106] Environmental Monitoring Near Industrial Sites: Methylchloroform. EPA-560/6-77-025, U.S. Environmental Protection Agency, Washington, D.C., August 1977. 82 pp.

[107] Environmental Monitoring Near Industrial Sites: Trichloroethylene. EPA-560/6-77-024, U.S. Environmental Protection Agency, Washington, D.C., August 1977. 75 pp.

5% PAH, and 30% oxygenated hydrocarbons [50]. Aliphatic hydrocarbons and PAH have also been identified in natural gas flame soot using GC-MS preceded by capillary column GC [108].

Ambient air sample extracts were analyzed for the presence of polychloronaphthalenes (PCN's) using a GC-quadrupole mass spectrometer with computerized data acquisition. The instrument was operated in the multiple-ion detection mode. The presence of PCN's was confirmed from full-scan mass spectra or by monitoring the chlorine isotope ratio [77]. Volatile compounds generated from chicken manure were collected and analyzed by GC-MS. Various alcohols, ketones, esters, carboxylic acid, and dimethyl disulfide were found [75]. GC-MS has also been used for the analysis of hazardous organic compounds from combustion effluents [71] and the analysis of trace organics in ambient atmospheres [92]. Trace, hazardous, organic vapor pollutants in ambient atmospheres have been determined by capillary gas-liquid chromatography mass spectrometry. Twenty-one halogenated hydrocarbons were detected including the carcinogens, vinyl chloride and trichloroethylene and numerous oxygen, sulfur, nitrogen, and silicon compounds [76]. A similar procedure was employed to identify 147 organic compounds emitted from automobile interiors [86].

High resolution mass spectrometry (HRMS) has been frequently cited as being useful in identifying atmospheric pollutants. Analysis of the volatilized material from temperature-programmed automobile exhaust particulates by HRMS showed that aliphatics and aliphatic-substituted benzenes constituted 99% by volume of the total volatile organic matter associated with the particulates [50]. HRMS has also been a useful means of characterizing the organic fraction of urban aerosols. Compounds detected included phenols, aromatic carboxylic acids, and aliphatic dibasic acids. Quantitative accuracy, however, was limited. Some ambiguities were found in the assignment of origins of ions formed in the mass spectrometer [109].

HRMS has been used to identify bis(chloromethyl) ether in the atmosphere. In the high resolution mass spectrometric procedure, the collected organic material is desorbed into the reservoir of the mass spectrometer heated inlet system and then examined at high resolution. One part-per-billion of BCME can be determined.

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[108] Vick, R. D., and M. J. Avery. Extraction and Identification of Organic Materials Present in Soot from a Natural Gas Flue. Contract W-7405-ENG-82, Dept. of Energy, January 1978. 19 pp.

[109] Crittenden, A. L. Analysis of Atmospheric Organic Aerosols by Mass Spectroscopy. EPA-600/3-76-093, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina August 1976. 296 pp.

The difficulties with the method are 1) chloromethyl methyl ether gives the same ion, 2) control of adsorption and regeneration effects, and 3) possible decomposition of BCME in the reservoir and its associated values [50].

HRMS was used to identify the major PAH compounds in samples obtained from fuel conversion process emissions. The analysis considered 14 highly carcinogenic PAH having nine unique formulas. Additional quantitative data were obtained by low ionizing voltage techniques [55]. HRMS combined with GC/MS and auxiliary techniques such as stable isotopic labeling, has been employed to illustrate the application of automated, real-time MS in the study of atmospheric organic pollutants [110]. Additionally, dioxirane has been detected in the gas phase by means of photoionization mass spectrometry [111].

Visible and Near Visible Spectrum Measurement Techniques--Ultraviolet (UV) infrared (IR) spectra have been used to identify atmospheric organics [52, 112]. Ultraviolet visible absorption spectrophotometry has been used in the analysis of B(a)P and other PAH following column chromatography. However, a more selective and faster method of analysis for B(a)P is the GC-UV absorptiometric method which has been used to analyze the PAH of auto exhaust and coke oven effluents [50].

Fourier-transform IR spectrometry has been employed to study the organic species participating in photochemical smog formation.

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[110] Simoneit, B. R., D. H. Smith, and G. Eglinton. Application of Real-Time Mass Spectrometric Techniques to Environmental Organic Geochemistry: I. Computerized High Resolution Mass Spectrometry and Gas Chromatograph - Low Resolution Mass Spectrometry. Archives of Environmental Contamination and Toxicology, 3(4):385, 1975-1976.

[111] Martinez, R. I., R. E. Huie, and J. T. Herron. Mass Spectrometric Detection of Dioxirane, H_2COO, and Its Decomposition Products, H_2 and CO, from the Reaction Ozone with Ethylene. Chemical Physics Letters 57(3):457-459, November 1977.

[112] Mendenhall, G. D., P. W. Jones, P. E. Strup, and W. L. Margard. Organic Characterization of Aerosols and Vapor Phase Compounds in Urban Atmospheres. EPA-600/3-78-031, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1978. 81 pp.

Product analyses of ozone-olefin reactions at ppm levels have been made by means of computer-aided subtraction techniques [113].

IR spectroscopy has also been used for the preliminary screening of chemical classes in air samples from combustion effluents [71]. An IR technique has been used for determining the nonvolatile organic matter associated with airborne particulates [114]. Recently developed, portable, IR gas analyzers have been used on solvent-laden atmospheres. Because all organic compounds have characteristic IR spectral lines, the analyzer can be used to detect and measure essentially all of the organic materials listed in the OSHA standards [115].

Fluorescence spectroscopy has been used frequently but has also exhibited problems in instrumental reproducibility, quenching phenomena, excimer formation (as evidenced by a change in the intensity and broadness of the usual emission spectral band), sensitized fluorescence, and photooxidation. One of the most specific and most sensitive methods for B(a)P involves its fluorescence in concentrated sulfuric acid. Preliminary separation can be by PC, TLC, GC or liquid-liquid extraction, dependent on the type of sample being analyzed. It has been recommended that in the TLC method alumina-coated aluminum foil sheets be used and the sulfuric acid solvent be purged with nitrogen before fluorimetric measurement. The advantages of fluorescence analysis in the analysis of B(a)P and other PAH are the greater senstivity the method and sometimes the increase in selectivity as compared to absorption spectral methods of assay. Low temperature fluorescence methods are also available for the analysis of B(a)P and other PAH. Quasi-linear spectra are obtained at liquid nitrogen temperatures. Since much fine structure is obtained, the method is capable of unequivocal characterization of B(a)P. By combining the high resolution of the spectrofluorimeter with that of the gas chromatograph, highly selective methods for B(a)P are possible. A GC-gas phase fluorescence instrument has been developed for such analyses and utilized in the analysis of a variety of mixtures [50].

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[113] Niki, H., P. Maker, C. Savage, and L. Breitenbach. Participating in Photochemical Smog Formation. Ford Motor Company, Dearborn, Michigan. International Conference on Environmental Sensing and Assessment, Las Vegas, Nevada, 14-19 September 1975. Published by IEEE, New York, Vol. 2, Paper 24-4, 1976. 4 pp.

[114] Della Fiorentina, H., J. Degraeve, and F. Dewiest. Determination of Non-Volatile Organic Matter Associated with Airborne Particulates by Infrared Spectrometery - 1. Operating Conditions. Atmospheric Environment, 9(5):513, May 1975.

[115] Kuhlman, C. M. Monitoring Toxic Air Contaminants. Plant Engineering, 31(15):149-150, 21 July 1977.

An immumoassay method with instrumentation has been developed for the detection of organic contaminants of environmental concern. The basic technique utilizes an antibody to the contaminant of concern with subsequent detection by means of fluorescence polarization or intensity measurements. Successful assays have been developed for diquat, hexachlorophene, and diethylstilbestrol [116]. A fluorescence spot test has been devised for PAH based on the sensitization of the inherent fluorescence of such compounds. The basic procedure involves spotting a filter paper with sample solution, adding naphthalene to the spot, and visually observing the fluorescence under UV illumination. In the case of B(a)P, one picogram has been detected. The method is specific for PAH with minimum interferences and can be used to estimate the general level of PAH within a factor of 10 [117].

PAH present in atmospheric particulate matter has also been analyzed using high pressure liquid chromatography coupled with on-line fluorescence detection [118]. Laser-excited matrix isolation fluorescence spectrometry is being developed as an analytical technique for characterizing polycyclic organic matter (POM) with special emphasis on the characterization of chemical carcinogens present in coal liquids and shale oil [119]. Both fluorescence and chemiluminescence techniques have been proposed to detect toxic air pollutants such as nitrogen dioxide, ozone, formaldehyde, halogens, hydrogen halides, hydrogen peroxide, and organic peroxides. Each of these pollutants undergoes photolysis in the solar region or the near-ultraviolet [120]. A chemiluminescent technique has been developed to determine the photochemical reactivity of organic pollutants in gaseous mixtures such as air, engine exhausts, and organic solvent vapors. In this method, the pollutants react with oxygen atoms to produce chemiluminescence which results in radiation emitted at two separate wavelengths and the difference in intensity is measured [121].

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[116] Lukens, H. R., C. B. Williams, S. A. Levinson, and W. B. Dardliker. Sensitive, Specific Fluorescence Immunoassay Methods for Detecting Pesticides and Other Organic Environmental Contaminants Arising from Biological or Chemical Sources. NSF/RA-770472, National Science Foundation, Washington, D.C., 21 November 1977. 95 pp.

[117] Smith, E. M., and P. L. Levins. Sensitized Fluorescence for the Detection of Polycyclic Aromatic Hydrocarbons. EPA-600/7-78-182, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1978. 31 pp.

[118] Foo, M. A., and S. W. Staley. Determination of Polycyclic Aromatic Hydrocarbons in Atmospheric Particulate Matter by High Pressure Liquid Chromatography Coupled with Fluorescence Techniques. Analytical Chemistry, 48(7):992-998, June 1976.

[119] El, W. Laser-Excited Matrix-Insulation Fluorometric Analysis of Polycyclic Aromatic Hydrocarbons. Grant CH77-12542, National Science Foundation, Washington, D.C., 1978.

Atomic absorption (AA) has been employed in the analysis of organic air pollutants. Organotin compounds have been detected in air at 0.1 mg/m^3 levels employing AA after concentration on silica gel and separation by chromatography [122]. A GC-AA apparatus has been mentioned earlier which measures the release of organometallic species, such as trimethylarsenic, from aquatic sediments [103]. The results of several studies in spectral methods are presented in Table A-3 [123].

Electrochemical Techniques--

Oxidation of odorous vapors at the anode of an electrochemical cell was studied as an approach to the analysis of odors. The technique of linear, potential sweep cyclic voltammetry was used to investigate the oxidizability of several amines, sulfides, and their mixtures. The results indicate that a mixture of sulfides and amines can be characterized [124]. A portable hydrazine

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[120] Hodgeson, J. A., and W. A. McClenny. Analytical Technique for Gaseous Pollutants Based on Photolysis and Detection of Primary Fragements. Presented in American Chemical Society, Division of Water, Air and Waste Chemistry, 28 August - 1 September 1972, Preprint 12-2.

[121] Fontijn, A. Chemiluminescent Method and Apparatus for Determining the Photochemical Reactivity of Organic Pollutants in a Gaseous Mixture. Patent Application 548,471 (U.S. Environmental Protection Agency), filed 10 February 1975. 21 pp.

[122] Riggle, C. J., D. L. Sgontz, and A. P. Graffeo. The Analysis of Organotins in the Environment. In: 4th Joint Conference on Sensing of Environmental Pollutants, New Orleans, Louisiana, 6-11 November 1977. p. 761.

[123] Hermann, T. S. Development of Sampling Procedures for Polycyclic Organic Matter and Polychlorinated Biphenyls. EPA-650/2-75-007, U.S. Environmental Protection Agency, Washington, D.C., August 1974.

[124] Nwankwo, J. N., and A. Turk. Electrochemical Analysis of Sulfidic and Amine Odorants. EPA-600/2-76-021, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1976. 46 pp.

TABLE A-3. SUMMARY OF SOME INVESTIGATIONS IN SPECTRAL METHODS [74]

Method	Procedure	Compounds	Normal sensitivity-range
Ultraviolet	Benzene extraction	Benzo(α)pyrene	0 to 45 µg/1000 m^3 air
Ultraviolet	Hexane extraction	Benzo(α)pyrene	10^{-2} µg/mL
Ultraviolet	Column chromatography	Benzo(α)pyrene	1 to 6 µg/mL
Ultraviolet	Hexane extraction	Dibenzanthrene	0.5 to 5 µg/mL
Fluorescence	Pentane extraction	Perylene	0.3 µg/mL
		Anthracene	0.3 µg/mL
		Benzo(α)pyrene	0.4 µg/mL

electrochemical analyzer is being designed and built to measure trace quantities of hydrazine in air [125].

Other Techniques--
Thermal energy analysis has been employed to determine dimethylnitrosoamine in air. The technique is sensitive at the 1 µg/m^3 level [126].

A quartz piezolelectric crystal coated with a substrate has been used for the detection of small mass changes caused by selective adsorption of organophosphorous compounds and pesticides. Incorporation of the crystal into a variable oscillator circuit and measurement of the change in frequency of the crystal due to the increase in mass allowed a sensitive quantification of the compounds present down to the ppm level [127].

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[125] Shaw, M. Prototype Hydrazines Electrochemical Analyzer. Contract F33615-78-C-0607, Air Force School of Aerospace Medicine, Brooks Air Force Base, San Antonio, Texas, 1978.

[126] Fine, D. H., D. P. Roundbehler, E. Sawicki, K. Frost, A. Rounbehler, A. Silvergleid, and G. A. Demarrais. Determination of Dimethylnitrosoamine in Air, Water, and Soil by Thermal Energy Analysis: Validation of Analytical Procedures. Environmental Science & Technology, 11(6):577, June 1977.

[127] Scheide, E. P., and G. C. Guilbault. Piezoelectric Detectors for Organophosphorus Compounds and Pesticides. Analytical Chemistry, 44(11):1764-1768, September 1972.

A portable battery-operated instrument has been developed for monitoring hydrocarbons and other trace gases in industrial atmospheres by photoionization [128].

Other techniques include laser intracavity Raman cell, enzymatic systems for environmental monitoring, gas detection sensors, liquid crystals, microwave-induced emission spectroscopy, and direct-current polarography [129]. In one study, the application of the piperonal test to the benzene-soluble fraction of airborne particulates was investigated. Piperonal reacts with aromatic compounds to give a colored product, which obeys Beer's Law. The correlation coefficients between benzo(*a*)pyrene concentrations and the piperonal test was 0.95 and 0.89 for 174 urban and 25 nonurban samples, respectively [123]. In two other studies, thermochromic tests were used for determining the amounts of polynuclear compounds containing the fluorenic methylene group and polycyclic *p*-quinones. In both cases, borohydridies were used at reflux temperatures for color development. Identification limits ranged from 3 to 40 μg. A somewhat similar study was reported where 4-azobenzene-diazonium fluoroborate was used to develop color in the determination of aniline, naphthylamine, and anthramine derivatives. The identification limits were in the range of 2 to 20 μg [123].

Gas detector tubes are also available for the semiquantitative determination of a specific pollutant. These tubes can be used for monitoring workplace environments and waste gases from automobiles, industrial processes, etc. The instrument consists of a hand-operated pump that sucks a measured volume of air per stroke thrugh the detector tube which is inserted into the pump. The detector tube is calibrated, and the extent of color change in the tube indicates the quantity of pollutant present. Wolfgang Leithe gives a more detailed description of this analytical technique [130].

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[128] Driscoll, J. N., and F. F. Spaziani. Trace Gas Analysis by Photoionization. In: 21st Annual ISA Analytical Instrumentation Symposium, Philadelphia, Pennsylvania, 6-8 May 1975. p 111-114.

[129] Trace Analysis and Detection in the Environment. Presented at 6th Annual Symposium on Environmental Research, Edgewood Arsenal, Aberdeen Proving Ground, Maryland. 29 April - 1 May 1975. Published by Dept. of Army, Edgewood Arsenal, Aberdeen Proving Ground, Maryland, EO-SP-76001, 1976.

[130] Leithe, W. The Analysis of Air Pollutants. Ann Arbor Science Publishers, Ann Arbor, Michigan, 1971.

APPENDIX B

STANDARD SAMPLE GENERATION SYSTEM

OBJECTIVE

In order to evaluate the sorbent sampling systems used in this project, it was necessary to have a method for generating known concentrations of organic compounds in dynamic gas streams. MRC has developed a dynamic standard Sample Generation System based on the controlled syringe injection of organic liquids into a flowing stream of gas (N_2), vaporization, and subsequent dilution.

INSTRUMENT

The Sample Generation System is shown schematically in Figure B-1. The main frame of the system is a modified gas chromatograph (F&M Model 700) with its protective metal covering and detector removed. The oven [30 cm (12 in.) x 30 cm (12 in.)] is in a relocated position on the left side of the main frame. Of the four heated zones available on the original GC, one controls the oven temperature, two are used to separately control the temperature of the two three-port injection blocks, and the final zone is available for heating transfer lines used for direct interfacing with a detector in frontal analysis capacity studies. A pyrometer (Simpson 0-500°C), a selection switch, thermocouples, and necessary circuit modifications allow the monitoring of temperatures in the four zones.

An aluminum plate [45.7 cm (18 in.) x 46.4 cm (18 1/4 in.) x 0.6 cm (1/4 in.)] is attached to the main frame to the right of the oven to accommodate the syringe drives. Necessary bulk-head fittings, tees, toggle valves, needle valves, tubing, pressure gauges, and rotameters are used in the configuration indicated in the figure. Materials of construction for the flow system are either stainless steel or nickel, and the entire system is contained in a large exhaust hood [2.4 m (8 ft) x 1.2 m (4 ft) x 1.5 m (5 ft)] with front and rear access through double sliding doors. Flow control/sensing instrumentation, pressure gauges, and rotameters are mounted on a panel and rack assembly in the hood above the generation system.

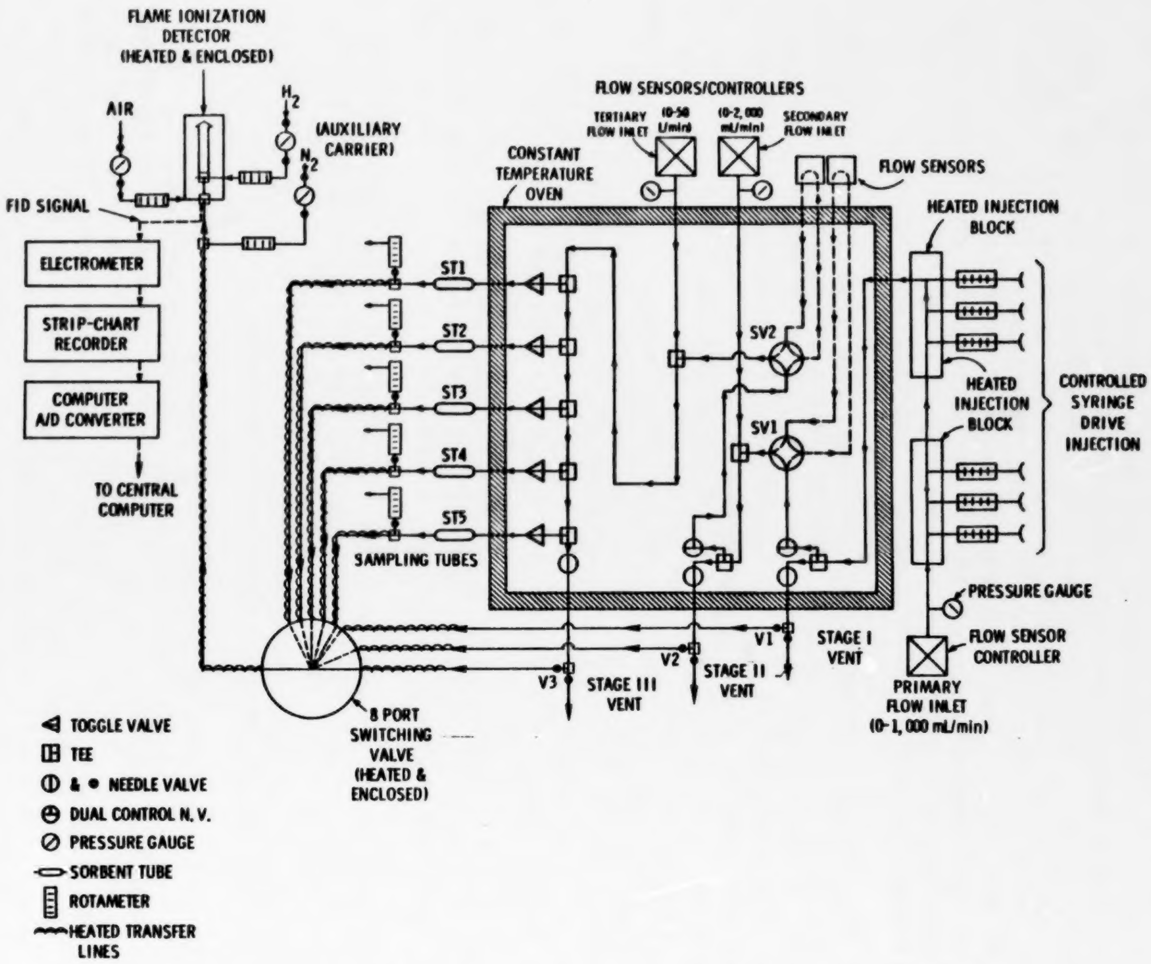

FLAME IONIZATION DETECTOR (HEATED & ENCLOSED)
AIR
H_2
N_2
(AUXILIARY CARRIER)
FID SIGNAL
ELECTROMETER
STRIP-CHART RECORDER
COMPUTER A/D CONVERTER
TO CENTRAL COMPUTER
FLOW SENSORS/CONTROLLERS
TERTIARY FLOW INLET
(0-50 L/min)
(0-2,000 mL/min)
SECONDARY FLOW INLET
FLOW SENSORS
CONSTANT TEMPERATURE OVEN
HEATED INJECTION BLOCK
HEATED INJECTION BLOCK
CONTROLLED SYRINGE DRIVE INJECTION
SV2
SV1
ST1
ST2
ST3
ST4
ST5
SAMPLING TUBES
PRESSURE GAUGE
FLOW SENSOR CONTROLLER
PRIMARY FLOW INLET (0-1,000 mL/min)
V1
V2
V3
STAGE I VENT
STAGE II VENT
STAGE III VENT
8 PORT SWITCHING VALVE (HEATED & ENCLOSED)
TOGGLE VALVE
TEE
& ● NEEDLE VALVE
DUAL CONTROL N. V.
PRESSURE GAUGE
SORBENT TUBE
ROTAMETER
HEATED TRANSFER LINES

Figure B-1. Standard Sample Generation System (SGS) with effluent monitor modification.

The Generation System functions in the following manner. A source of carrier gas (N_2) is introduced into the system and split into primary, secondary and tertiary flows. The primary flow passes through a mass-flow sensor/controller (Brooks Model 5841) which maintains the flow rate at a preset value (0-1,000 mL/min). This flow passes through individually heated and controlled injection blocks which are each designed to accept three syringes mounted on variable-control syringe drives (Sage Model 355). This permits the simultaneous introduction of six pure liquid components, or potentially many more, if mixtures of compounds are used in the syringes. The rate of injection can be varied from submicroliter/hour to milliliter/minute by the appropriate choice of syringe size and drive rate. Liquid samples are vaporized in the injection blocks and swept with the carrier gas into a constant temperature oven.

Most of the primary flow passes through the oven and through a needle valve used to regulate the pressure in the primary flow path. It is then expelled to the vent (V1). A small portion (usually ∿10 mL/min) of the primary flow is removed through a dual-control needle valve and passes into a switching valve (SV1) which is actually one-half of an eight-port switching valve. The second half of the switching valve is used for an identical function in the second dilution stage. The switching valve makes it possible to insert a mass-flow sensor (Brooks Model 5810, 0-100 mL/min) in the flow path (indicated by the dashed line in Figure B-1) to measure the exact split of the primary flow. Once the split has been established, the flow sensor is switched out of the system so that the sensing elements are not subjected to sample-containing organic vapors. The split is maintained by carefully controlling the pressures in each dilution stage.

Pressures are monitored with precision pressure gauges [Heise Model CM, 0-6.9 x 10^5 Pa (0-100 psi)]. By maintaining a constant pressure in each dilution stage, a constant pressure differential is established between the stages assuring a consistent split ratio across the needle valves.

The split-out portion of the primary flow passes from the switching valve and is combined with the secondary carrier flow which enters the constant temperature oven through a mass-flow sensor/controller (Brooks Model 4841, 0-2,000 mL/min). As in the case of the primary flow, most of the secondary flow passes through the oven and is expelled to the vent (V2) through a needle valve. A small portion (usually 10 mL/min) of the secondary flow is removed through a dual-control needle valve and passes into a switching valve (SV^2). This valve functions in an identical manner to SV1 and places a second mass-flow sensor (Brooks, Model 5810, 0-100 mL/min) in the flow path for measuring the second split.

The split-out portion of the secondary flow passes from the switching valve and is combined with the final (tertiary) dilution stream which enters the constant temperature oven through a mass-flow sensor/controller (Brooks Model 5841, 0-50 L/min). This final concentration is available for sampling through a five-port manifold system that will accommodate sorbent sampling tubes. Sampling rates through the sorbent tubes are maintained by rotameters (Brooks Model 1110) at the tube exits. The unused portion of the final dilution stage is expelled to the vent (V3).

The sample generation system is connected through an eight-port (Valco) selection valve and stainless-steel tubing [1.6 mm (1/16 in.)] to a flame ionization detector. This arrangement permits the selective monitoring of concentration levels in each of the three dilution stages and the additional monitoring of effluent from five sampling locations.

Evaluation studies have demonstrated linear concentration responses over the operational ranges of the syringe drive rate, the two split monitors, and the three dilution stages. By the appropriate selection of syringe size, drive rate, split ratios, and dilution rates, it is possible to achieve continuously variable concentrations from percent to low part-per-trillion levels using this system.

APPENDIX C

OPERATION MANUAL

PURPOSE

The purpose of this manual is to provide the information necessary to construct, prepare, calibrate, and operate the ambient air collection system which was designed, under EPA contract 68-02-2773, to collect and concentrate a certain number (15 to 20) of selected compounds of potential carcinogenic nature from ambient air for later analytical assessment.

PREPARATION, CLEANING, AND CONDITIONING OF REPLACEABLE SORBENT CARTRIDGES

The ambient air collection system is comprised of two major parts: the sorbent tube tray, which contains replaceable sorbent cartridges that collect and concentrate organic vapors from an air stream passing through them; and the Nutech Model 221-1A Air Sampler, which draws the air stream through the sorbent tube tray. This section will provide the procedures for preparing the replaceable sorbent cartridges for use in field sampling, while other aspects of preparing, calibrating, and operating the ambient air collection system will be discussed later in this manual.

Cleaning of Sorbent Materials

The replaceable sorbent cartridges used within the ambient air collection system's tube tray consist of three types, each type containing a different sorbent material (Tenax-GC, Porapak R, and Ambersorb XE-340). These sorbents are listed in Table C-1 along with other pertinent information. They may be obtained from their manufacturers, or Tenax-GC and Porapak R may be obtained from a chromatography supply distributor (e.g., Supelco, Alltech, Applied Science, etc.).

Generally, all commercial sorbent materials as received from suppliers contain significant levels of background contamination as the result of production, packaging, and/or transportation. To prepare the sorbent materials for cartridge sampling, their backgrounds must be reduced to minimal levels and then maintained at these levels. To start, one can remove most of the initial contamination from the sorbent materials by an extensive solvent cleanup. The procedure for this solvent cleanup is given below:

TABLE C-1. PERTINENT SORBENT INFORMATION

Information	Sorbent		
	Tenax-GC	Porapak R	Ambersorb XE-340
Mesh size	35/60 mesh	50/80 mesh	?
Manufacturer's temperature limit	350°C	250°C	>350°C
Conditioning temperature	325°C	230°C	325°C
Desorption temperature	300°C	≤200°C	300°C
Desorption time	30 min	60 min	60 min
Physical description	off-white powder	off-white sphere	black, shiny sphere
Amount packed in a cartridge	0.9 to 1.1 g	1.6 to 1.8 g	3.0 to 3.4 g
Chemical composition	2,6-diphenyl-p-phenylene oxide	N-vinyl pyrrolidone	styrene-divinyl benzene
Major thermal decomposition products	alkyl benzenes, styrene, benzene, alkyl phenols	vinyl pyrrolidone, pyrrolidone	styrene, benzene, alkyl benzenes
Solvent incompatability	chlorinated solvents	?	?
Manufacturer address	Enka, Inc. Netherlands	Waters Associates Milford, MA	Rohm & Haas Philadelphia, PA

1) Soxhlet extract sorbent for 16 to 24 hr with distilled-in-glass (high-purity) methanol.

2) Vacuum dry sorbent at 120°C and approximately 1.02×10^5 Pa (30 in Hg) vacuum for 16 to 24 hr.

3) Soxhlet extract sorbent for 16 to 24 hr with distilled-in-glass (high-purity) pentane.

4) Vacuum dry sorbent at 120°C and approximately 1.02×10^5 (30 in Hg) vacuum for 16 to 24 hr.

5) Store sorbent in a clean glass jar with a screw-on cap within a dessicator.

At this point the sorbent is clean enough to be loaded into glass cartridge tubes (which will be discussed later), and may be stored for a few months (~3 to 6 months) without re-extraction as long as it is protected from contaminants. Sorbent may also be stored for several weeks under solvent after one of the extraction procedures and prior to vacuum drying, if desired.

The purpose of this sorbent cleanup procedure is to remove most contaminants from the sorbent material; however, contaminants may also be added during this cleanup procedure, such as from trace impurities present in the solvent, if one is not careful to prevent such contamination. Therefore, one should always use high-purity solvents and clean glassware during soxhlet extractions, and the glass joints should be sealed with Teflon tape or Teflon sleeves (not with silicone grease). Furthermore, a small charcoal trap should be used in the vacuum line of the vacuum oven to prevent the contamination of the drying sorbent material by the back-diffusion of vacuum-pump lubricants.

Preparation of Glass Cartridge Tubes

In addition to cleaning the sorbent materials which are contained within the replaceable sorbent cartridges, the glass cartridge tubes must also be appropriately prepared. The first step of this preparation is to make these tubes (using pyrex glass) according to the specifications given in Figure C-1. This tapered cartridge design has been found to allow an appropriate compromise of sorbent cartridge properties, such that pressure drop is kept to a minimum, thermal desorption and sorbent capacity properties are kept to a maximum, and the sorbent material is adequately contained. (The reasoning behind the selection of this sorbent cartridge design is more thoroughly discussed in the final report of this contract.) During the manufacture of these glass cartridge tubes, each tube should be numbered (at one end, as indicated in Figure C-1) to permit easy identification of sorbent cartridges for record-keeping and sampling purposes. These numbers should

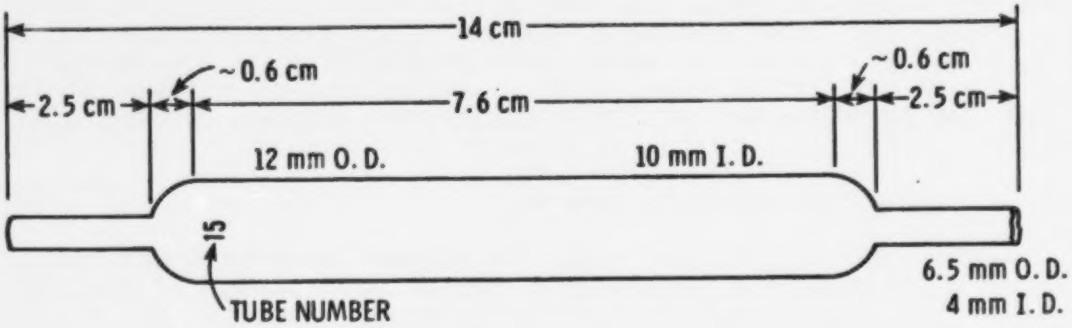


Figure C-1. Specifications of selected sampling tube design.

be able to withstand high temperatures (400°C) and should not be washed off by common laboratory solvents (acetone, methanol, toluene, methylene chloride, or pentane). Ceramic numbers annealed to the glass at +400°C have been found to be quite suitable. Preferably, the numbers should be a distinct bright color, such as red, although other colors are permissible as long as they can be distinguished.

Once the glass cartridge tubes have been constructed, they may be stored indefinitely in their empty condition. However, before sorbent is packed within them, the glass tubes should undergo the cleaning and deactivating procedures listed below.

1) Clean glass tubes in a heated ultrasonic bath containing glassware detergent (e.g., Microclean, LiquiNox, etc.) for 4 to 8 hr, or meticulously "hand-clean" with glassware detergent and a soft test tube brush.

2) Rinse interior and exterior with methanol (reagent grade).

3) Bake tubes dry at 300°C to 400°C for 8 to 16 hr.

4) Prepare a 10% solution of dimethyldichlorosilane in high-purity, distilled-in-glass toluene (deactivating solution).

5) Soak glass tubes in deactivating solution for at least 15 min.

6) Thoroughly rinse tubes with high-purity, distilled-in-glass methanol.

7) Bake tubes dry at ~300°C for 8 to 16 hr.

8) Store glass tubes in a clean, dry environment.

While following the procedures just described, care should be taken to avoid contaminating the tubes (with fingerprints, etc.). Therefore, the tubes should always be handled while wearing protective gloves and/or with clean utensils (e.g., tweezers, tongs, etc.). Furthermore, after cleaning and deactivating, the tubes should be packed with the appropriate sorbent material(s) within a reasonable period of time (~ one month).

Cleaning of Other Hardware Materials

The other materials (other than the sorbent materials and glass tubes) which are used in the preparation and storage of the replaceable sorbent cartridges include glass wool, which is used to contain sorbent within the glass cartridges, and stainless steel fittings, viton o-rings, and culture tubes, which are used to seal and store the sorbent cartridges.

Generally, glass wool as received from a chromatography supply distributor (e.g., Supelco, Alltech, Applied Science, etc.) should be clean enough for packing the sorbent cartridges since little of this material is used and the sorbent cartridges are conditioned after packing. The type of glass wool ordered should be a soft, fine pyrex wool which has been silanized (preferably with dimethyldichlorosilane). If the glass wool which is available is probably contaminated (through use), then either new glass wool should be ordered or the contaminated glass wool should undergo the following procedures.

1) Soxhlet extract glass wool for 16 to 24 hr with high-purity distilled-in-glass methanol.

2) Vacuum dry glass wool at 120°C and approximately 1.02×10^5 Pa (30 in. Hg) vacuum for 16 to 24 hr.

3) Soxhlet extract glass wool for 16 to 24 hr with high-purity distilled-in-glass pentane.

4) Vacuum dry glass wool at 120°C and approximately a 30 in. Hg vacuum for 16 to 24 hr.

5) Prepare a 10% solution (deactivation solution) of dimethyldichlorosilane in high-purity, distilled-in-glass toluene.

6) Soak the glass wool in the above deactivating solution for at least 30 min.

7) Soxhlet extract glass wool for 8 to 16 hr with high-purity, distilled-in-glass methanol.

8) Vacuum dry glass wool at 120°C and approximately 1.02×10^5 Pa (30 in. Hg) vacuum for 24 to 48 hr.

As previously discussed during the cleaning of the sorbent materials, the extraction glassware should be clean; Teflon tape or Teflon sleeves should be used at the glass joints instead of silicone grease; and a charcoal trap should be used in the vacuum line of the vacuum oven to prevent contamination of the glass wool by the back-diffusion of vacuum-pump lubricants. This procedure, however, has been found to create a problem with silicon contamination due to excess silanizing reagent retained on the glas wool. Blank analyses of glass wool, therefore, should be performed to determine whether it is suitable for packing sorbent tubes. If unacceptable, the extraction and drying procedures should be repeated.

After the glass cartridges are packed with the sorbent materials (which will be discussed later), the sorbent cartridges are sealed with stainless steel fittings and viton o-rings, and placed within pyrex culture tubes (200 mm long by 25 mm diameter) with Teflon-lined, screw-on caps for storage (as depicted in Figure C-2). Since these materials are to be used to protect the sorbent cartridges from atmospheric contaminants, they should be prepared in such a manner that they introduce minimal contaminants to the sorbent cartridges. To do so, the viton o-rings, stainless steel fittings, pyrex culture tubes, and the Teflon-lined, screw-on culture tube caps should be cleaned according to the procedures listed below.

1) Clean indicated items in a heated ultrasonic bath containing glassware detergent (e.g., Microclean, LiquiNox, etc.) for 4 to 8 hr.

2) Thoroughly rinse these materials with high-purity, distilled-in-glass methanol.

3) Bake items dry at ~120°C for 8 to 16 hr.

4) Store items in a clean, dry environment until used.

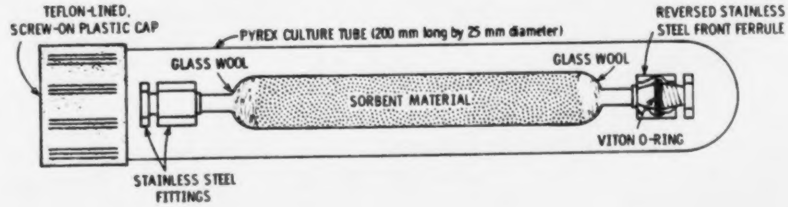

TEFLON-LINED, SCREW-ON PLASTIC CAP
PYREX CULTURE TUBE (200 mm long by 25 mm diameter)
REVERSED STAINLESS STEEL FRONT FERRULE
GLASS WOOL
GLASS WOOL
SORBENT MATERIAL
VITON O-RING
STAINLESS STEEL FITTINGS

Figure C-2. Materials used to seal and store a sorbent cartridge.

Preparation of Sorbent Cartridges

With the sorbent materials solvent cleaned, and dried, the glass cartridge tubes cleaned and deactivated; and the other hardware materials (glass wool, stainless steel fittings, etc.) cleaned; all the required materials are ready for the sorbent cartridges to be prepared for sampling. This preparation consists of two major steps: (1) packing the sorbent tubes and (2) thermally conditioning them to remove most remaining contaminants, thereby reducing their backgrounds to minimal levels.

To pack a sorbent cartridge the procedures given below should be followed, with all weights carefully recorded (this will be discussed more thoroughly later).

1) Weigh an empty glass cartridge tube.

2) Weigh two small pieces of glass wool (~10 to 20 mg each).

3) Place one piece of glass wool into the glass cartridge tube at one of the tapered ends just before the 6 mm O.D. portion of the tube (see Figure C-3A).

4) Draw a vacuum at this end of the sorbent tube (see Figure C-3B).

5) Place several grams of one of the three sorbent materials in a clean, shallow, glass container (e.g., watch glass, petri dish, etc.).

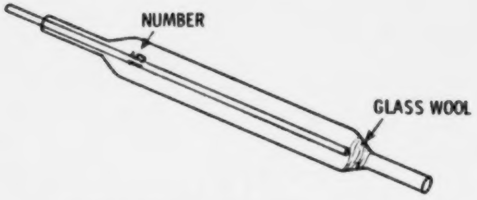
6) "Vacuum" the sorbent material into the glass cartridge tube until just a small space is left at the unplugged tapered end just before the 6 mm O.D. portion of the tube (see Figure C-3C and C-3D).

7) Remove the vacuum and place the remaining piece of glass wool at the other end of the tube (see Figure C-3E).

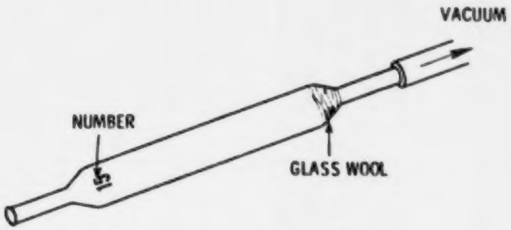
8) Weigh the sorbent cartridge and determine the amount of sorbent within the cartridge.

9) Modify the amount of sorbent placed within the cartridges to try to attain the sorbent quantities specified in Table C-1 (0.9 to 1.1 g of Tenax-GC, 1.6 to 1.8 g of Porapak R, and 3.0 to 3.4 g of Ambersorb XE-340).

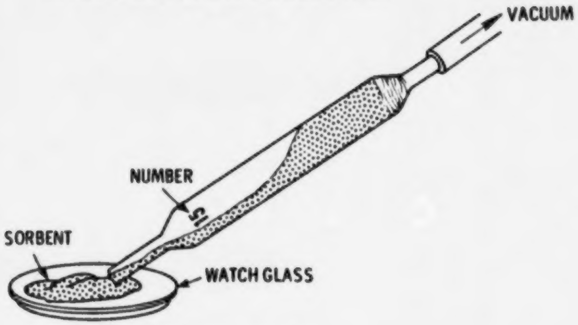
While packing the sorbent cartridges as just described, care should be taken to avoid extraneous contamination of the sorbent materials, glass wool, or glass cartridge tubes. Therefore, as previously indicated, all materials should be handled while wearing protective gloves and/or with clean utensils (e.g., tweezers, tongs, etc.). The vacuum line should include a charcoal trap to


NUMBER
GLASS WOOL

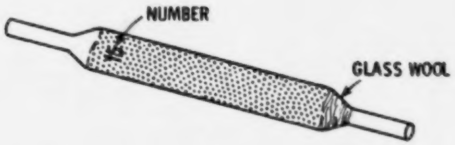
A. PLACE GLASS WOOL AT ONE TAPERED END.


VACUUM
NUMBER
GLASS WOOL

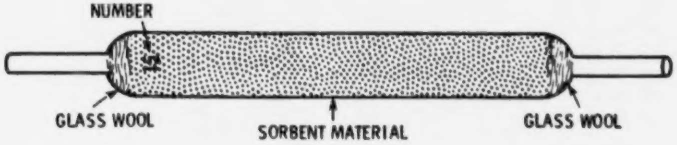
B. ATTACH TUBE TO A VACUUM.


VACUUM
NUMBER
SORBENT
WATCH GLASS

C. "VACUUM" SORBENT INTO TUBE.


NUMBER
GLASS WOOL

D. LEAVE ROOM FOR OTHER GLASS WOOL PLUG.


NUMBER
GLASS WOOL
SORBENT MATERIAL
GLASS WOOL

E. PLACE REMAINING GLASS WOOL AT UNPLUGGED TAPERED END.

Figure C-3. Procedure for packing a sorbent cartridge.

prevent contamination by the back-diffusion of pump lubricants. Generally, these procedures may be followed in the open laboratory. Although, the sorbent will quickly adsorb vapors present in the lab air, the thermal conditioning procedure should remove these contaminants. However, if a clean-box or clean-room is available, then these facilities would be preferred while packing the sorbents since a clean, inert atmosphere would further reduce potential background and contamination.

After the sorbent cartridges have been packed, they need to be thermally conditioned to remove most remaining contaminants thereby reducing their backgrounds to minimal levels and making them suitably clean for sampling. The current technique which is used to condition sorbent cartridges has been found to be adequate for most sampling applications.

The sorbent cartridge thermal conditioning technique is straightforward and simply involves passing a purified, inert stream of gas (helium or nitrogen) at ~30 mL/min through a sorbent cartridge for 16 to 24 hr with the sorbent cartridge within an oven heated to an appropriate temperature (230°C for Porapak R, and 325°C for Tenax-GC and Ambersorb XE-340). The gas stream should be purified by placing a drierite trap, a molecular sieve trap, and a charcoal trap in the gas stream (in that order) before passing the gas stream through the sorbent cartridges. This gas stream is then attached to a manifold comprised of stainless steel fittings and contained within a laboratory oven (with a maximum temperature of $\geq$325°C). A small section of such a manifold is sketched in Figure C-4, shown with a few sorbent cartridges attached. A manifold of this type can be extended to condition as many tubes as there is room for within the laboratory oven, as long as a flow rate of ~30 mL/min can be attained through the tubes. The tubes are connected to the manifold using graphite ferrules.

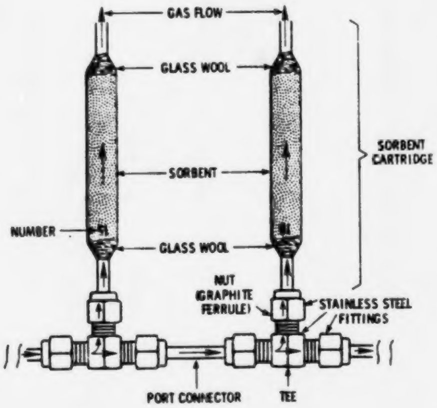


Figure C-4. Section of manifold used for thermally conditioning sorbent cartridges.

The critical portion of this sorbent cartridge thermal conditioning technique occurs after the cartridges have been purged with purified gas in a heated environment and are ready to be removed from the conditioning manifold to be stored for later sampling. As mentioned previously, sorbent will quickly adsorb vapors present in the lab air. This will occur as soon as thermal conditioning is stopped (i.e., heat and purge gas are turned off). Therefore, it is imperative that the sorbent cartridges be sealed from contaminating laboratory atmosphere as soon as possible after thermal conditioning is discontinued. When the sorbent cartridges are barely cool enough to be handled (while wearing protective gloves and/or using clean utensils), the nuts (with graphite ferrules) which are used to connect the cartridges to the manifold should be carefully (the cartridges easily break while hot) loosened. As rapidly as possible the sorbent cartridges should then be removed by slipping them out of the manifold nuts and then sealed with metal fittings and o-rings (as shown previously in Figure C-2). After all the sorbent cartridges are sealed in this manner, they should be placed inside individual culture tubes and the culture tubes sealed with their Teflon-lined, screw-on plastic caps (see Figure 2). These sorbent tubes are now properly prepared for collecting samples.

To assure the sorbent backgrounds are at their minimal levels, sampling should be done as soon as possible after the tubes are conditioned (preferably ≤ one week). Tubes stored for more than ~one week should again be thermally conditioned prior to sampling. Any labels which are used to designate the samples the sorbent cartridges are to be used to collect (or blanks, etc.) should be affixed to the outside of the culture tube to prevent the ink or adhesive from contaminating the sorbent. Finally, if rough handling is anticipated, especially during transportation, clean glass wool should be placed within the culture tube surrounding the sorbent cartridge to offer the cartridge additional cushioning and protection from breakage.

Storage, Background, and Contamination

As mentioned several times previously, precautions should be taken to prevent contamination of a sorbent cartridge during its preparation. These precautions include handling all materials while wearing protective gloves and/or using clean utensils, using high-purity, distilled-in-glass solvents, using Teflon-tape or Teflon-sleeves instead of silicone grease at soxhlet extractor glass joints, placing a charcoal trap in the vacuum line of a vacuum oven system to prevent the contamination of drying materials by the back-diffusion of pump lubricants, and many others (which have been previously stated). The purpose of cleaning the sorbent and other materials, taking precautions to prevent contamination during sorbent cartridge preparation, and conditioning the sorbent cartridges within ~one week of sample collection is to assure that the sorbent cartridges have minimal levels of background and contamination.

It should be noted here, however, that although contamination can contribute to the background (materials present during a sorbent cartridge analysis when no materials have been added to the cartridge [i.e., a blank]) present on a sorbent cartridge, background can also be contributed by the sorbent material through slow degradation (or "aging"). For this reason a sorbent cartridge should be reconditioned just prior to sampling if it has been stored for more than ~one week. However, the thermal or chemical decomposition of a sorbent caused by sampling/analytical conditions also can significantly contribute to sorbent cartridge backgrounds. Thermal decomposition of a sorbent results, of course, from overheating the sorbent cartridge during conditioning, sampling, or desorption. Therefore, not exposing the sorbent cartridges to temperatures above their temperature limits (given in Table C-1) should minimize thermal decomposition problems. Chemical decomposition caused by exposing the sorbent cartridges to inappropriate solvents (also given in Table C-1) should also be avoided. Chemical decomposition may also be caused by reactive species (such as NO_x, SO_2, and HCl) in the sample matrix (which if anticipated can be potentially removed by selective filters placed prior to the sorbent cartridge), but they should not present a major problem with ambient air samples.

Usually, the analyses of "blank" sorbent cartridges is enough to indicate the type of compounds and their levels which comprise the sorbent background. Quite often, background (of a particular sorbent) from many "blank" tubes vary somewhat in their amounts, as indicated by peak sizes (or areas), but retain a certain pattern (i.e., peaks from various analyses have similar retention times and similar chemical type). This pattern is probably due to compounds produced by sorbent decomposition which is typical for that particular sorbent because of the chemical composition of the sorbent. For example, Table C-1 lists some of the major thermal decomposition products that might be expected for the sorbent materials used for this project based on their chemical composition (also given in Table C-1). Knowing the types of decomposition products to expect from a particular sorbent, one can determine whether thermal or chemical decomposition of the sorbent likely occurred during sample collection, such as from matrix effects. Therefore, one can evaluate whether the compounds detected during an analysis of a sorbent cartridge sample are the result of the collected sample or some type of sorbent decomposition.

Records

It was briefly noted when discussing the packing of the sorbent cartridges that records should be kept of all glass cartridge tube and sorbent weights. Indeed, the reason that numbers are to be permanently annealed to the glass cartridge tubes is for record-keeping purposes. It is essential that accurate histories be kept for each sorbent tube in order to assure the quality control of all sorbent cartridge samples. Therefore, the sorbent cartridges must be marked in some manner (the annealed numbers) in order to assure individual identification. Furthermore, all manipulations of the sorbent cartridge or the sorbent material, including weights, cleanup and conditioning procedures, and storage times, need to be recorded and associated with each sorbent cartridge. By keeping such accurate histories of each sorbent cartridge, one avoids such poor quality control situations as trying to compare the results of two duplicate samples, one collected on a freshly packed sorbent cartridge and the other collected on a sorbent cartridge in use for at least five years. Obviously, a great disparity of results could be caused by the difference in "age" and treatment of the two sorbent cartridges. In addition, such recordkeeping helps to prevent the possibility of getting different types (i.e., packed with different sorbent materials) of sorbent cartridges mixed-up and overheating some during conditioning because the wrong thermal conditioning temperature was used. For example, if a few Porapak R sorbent cartridges are conditioned with a number of Tenax-GC sorbent cartridges at the conditioning temperature of Tenax-GC (325°C), the temperature limit of the Porapak R sorbent cartridges (250°C) would be exceeded and the Porapak R would thermally decompose. Therefore, the history of each sorbent tube should be kept meticulously, beginning with the "initiation" of the sorbent cartridge, which should include sorbent cleanup procedures, sorbent cartridge weights, and conditioning information; continuing through the sorbent cartridge's "sampling lifetime," which should include storage, packaging, and transportation information, sampling conditions and dates, and analytical log-in numbers, procedures, and results; and ending with the "termination" of the sorbent cartridge, which should include the procedure and date the cartridge was either reconditioned or unpacked. All of this information should be kept on each sorbent cartridge according to its annealed number and retained within a sorbent history log book. Figure C-5 depicts the information which should be kept within the log book associated with the "initiation" of each sorbent cartridge, information which should be entered while following the procedure in this section of this Operation Manual. The records associated with the aspects of a sorbent cartridge's "sampling lifetime" and "termination" will be further discussed later in this manual.

FLOW CHART

For convenience, a flow chart which summarizes the procedures for the preparation, cleaning, and conditioning of the replaceable sorbent cartridges is given in Figure C-6.

Name:

Tube #: Sorbent Type: Date Packed:

Weight of: Glass Cartridge: Glass Wool: Sorbent:

Sorbent Material Information

Supplier: Mesh Size: Lot #:

Date Opened: Date Arrived: Generation: 1 2 3

Cleanup Procedure:

Cleanup Dates:

Sieve Size: Sieve Date:

Storage Procedures and Conditions:

Storage Dates:

Storage Procedures and Conditions:

Storage Dates:

Sorbent Cartridge Conditioning

Date Packed: Storage Procedure & Dates:

Conditioning Procedure:

Conditioning Date:

Conditioning Procedure:

Conditioning Date:

Conditioning Procedure:

Conditioning Date:

Conditioning Procedure:

Conditioning Date:

Figure C-5. Information which should be recorded in the sorbent cartridge logbook.

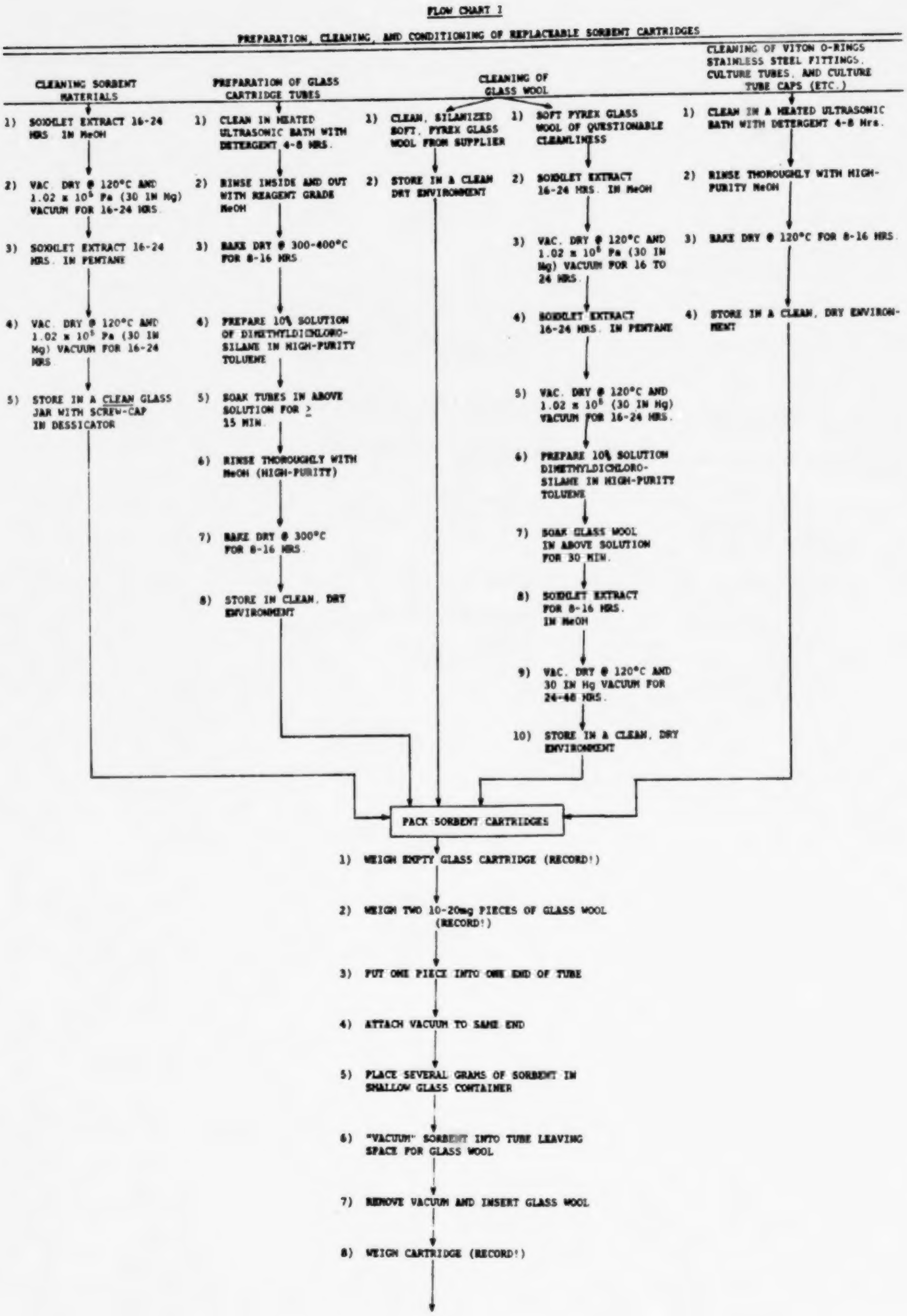

FLOW CHART I
PREPARATION, CLEANING, AND CONDITIONING OF REPLACEABLE SORBENT CARTRIDGES
CLEANING SORBENT MATERIALS
1) SOXHLET EXTRACT 16-24 HRS. IN MeOH
2) VAC. DRY @ 120°C AND 1.02 x 10^5 Pa (30 IN Mg) VACUUM FOR 16-24 HRS.
3) SOXHLET EXTRACT 16-24 HRS. IN PENTANE
4) VAC. DRY @ 120°C AND 1.02 x 10^5 Pa (30 IN Mg) VACUUM FOR 16-24 HRS.
5) STORE IN A CLEAN GLASS JAR WITH SCREW-CAP IN DESSICATOR
PREPARATION OF GLASS CARTRIDGE TUBES
1) CLEAN IN HEATED ULTRASONIC BATH WITH DETERGENT 4-8 HRS.
2) RINSE INSIDE AND OUT WITH REAGENT GRADE MeOH
3) BAKE DRY @ 300-400°C FOR 8-16 HRS.
4) PREPARE 10% SOLUTION OF DIMETHYLDICHLORO-SILANE IN HIGH-PURITY TOLUENE
5) SOAK TUBES IN ABOVE SOLUTION FOR ≥ 15 MIN.
6) RINSE THOROUGHLY WITH MeOH (HIGH-PURITY)
7) BAKE DRY @ 300°C FOR 8-16 HRS.
8) STORE IN CLEAN, DRY ENVIRONMENT
CLEANING OF GLASS WOOL
1) CLEAN, SILANIZED SOFT, PYREX GLASS WOOL FROM SUPPLIER
2) STORE IN A CLEAN DRY ENVIRONMENT
1) SOFT PYREX GLASS WOOL OF QUESTIONABLE CLEANLINESS
2) SOXHLET EXTRACT 16-24 HRS. IN MeOH
3) VAC. DRY @ 120°C AND 1.02 x 10^5 Pa (30 IN Mg) VACUUM FOR 16 TO 24 HRS.
4) SOXHLET EXTRACT 16-24 HRS. IN PENTANE
5) VAC. DRY @ 120°C AND 1.02 x 10^5 (30 IN Hg) VACUUM FOR 16-24 HRS.
6) PREPARE 10% SOLUTION DIMETHYLDICHLORO-SILANE IN HIGH-PURITY TOLUENE
7) SOAK GLASS WOOL IN ABOVE SOLUTION FOR 30 MIN.
8) SOXHLET EXTRACT FOR 8-16 HRS. IN MeOH
9) VAC. DRY @ 120°C AND 30 IN Hg VACUUM FOR 24-48 HRS.
10) STORE IN A CLEAN, DRY ENVIRONMENT
CLEANING OF VITON O-RINGS STAINLESS STEEL FITTINGS, CULTURE TUBES, AND CULTURE TUBE CAPS (ETC.)
1) CLEAN IN A HEATED ULTRASONIC BATH WITH DETERGENT 4-8 Hrs.
2) RINSE THOROUGHLY WITH HIGH-PURITY MeOH
3) BAKE DRY @ 120°C FOR 8-16 HRS.
4) STORE IN A CLEAN, DRY ENVIRONMENT
PACK SORBENT CARTRIDGES
1) WEIGH EMPTY GLASS CARTRIDGE (RECORD!)
2) WEIGH TWO 10-20mg PIECES OF GLASS WOOL (RECORD!)
3) PUT ONE PIECE INTO ONE END OF TUBE
4) ATTACH VACUUM TO SAME END
5) PLACE SEVERAL GRAMS OF SORBENT IN SHALLOW GLASS CONTAINER
6) "VACUUM" SORBENT INTO TUBE LEAVING SPACE FOR GLASS WOOL
7) REMOVE VACUUM AND INSERT GLASS WOOL
8) WEIGH CARTRIDGE (RECORD!)

Figure C-6. Flow chart summarizing sorbent cartridge preparation procedures.

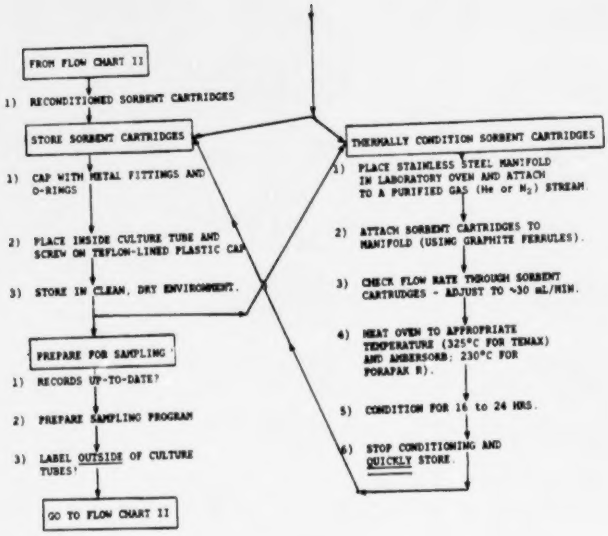

FROM FLOW CHART II
1) RECONDITIONED SORBENT CARTRIDGES
STORE SORBENT CARTRIDGES
1) CAP WITH METAL FITTINGS AND O-RINGS
2) PLACE INSIDE CULTURE TUBE AND SCREW ON TEFLON-LINED PLASTIC CAP
3) STORE IN CLEAN, DRY ENVIRONMENT.
PREPARE FOR SAMPLING
1) RECORDS UP-TO-DATE?
2) PREPARE SAMPLING PROGRAM
3) LABEL OUTSIDE OF CULTURE TUBES!
GO TO FLOW CHART II
THERMALLY CONDITION SORBENT CARTRIDGES
1) PLACE STAINLESS STEEL MANIFOLD IN LABORATORY OVEN AND ATTACH TO A PURIFIED GAS (He or N2) STREAM.
2) ATTACH SORBENT CARTRIDGES TO MANIFOLD (USING GRAPHITE FERRULES).
3) CHECK FLOW RATE THROUGH SORBENT CARTRUDGES - ADJUST TO ~30 mL/MIN.
4) HEAT OVEN TO APPROPRIATE TEMPERATURE (325°C FOR TENAX) AND AMBERSORB; 230°C FOR PORAPAK R).
5) CONDITION FOR 16 to 24 HRS.
6) STOP CONDITIONING AND QUICKLY STORE.

Figure C-6 (continued)

PREPARATION, CALIBRATION, AND OPERATION OF THE AMBIENT AIR COLLECTION SYSTEM

This section of this manual describes all aspects of the preparation, operation, and calibration of the ambient air collection system. Included are instructions on how to assemble the replaceable sorbent cartridges within a sorbent tube tray, how to operate the Nutech Air Sampler, how to calibrate the Nutech Air Sampler without and with a sorbent tube tray attached, and how to set up and monitor the ambient air sampling system. In addition, quality control, storage, recordkeeping, and other aspects of a field sampling program are discussed. This section should provide enough information for the collection of ambient air samples using replaceable sorbent cartridges, and the handling of these samples until analysis.

Operation and Calibration of the Nutech Model 221-1A AC/DC Air Sampler

The Nutech Model 221-1A AC/DC Air Sampler is an air pumping system which is used in the ambient air sampling system to draw an air stream through a sorbent tube tray. A major portion of the manufacturer's "Operating Manual: Model 221-1A, AC/DC Sampler for Remote Sample Collection Using Wet Chemical Collectors and Gas Chromatography Cartridges," is presented below with the permission of the Nutech Corporation. Sections, tables, and figures drawn from this manual are referenced. Metric values have been added and some minor corrections made.

INTRODUCTION [131]

The Model 221 gas sampler is optimally designed for remote sampling of hydrocarbon vapors using GC cartridges. The pumping system is powerful enough to provide 10 Lpm and a large pressure drop to accommodate a wide variety of cartridge collectors. However, the unit is small enough to be hand carried, and power requirements are within the range of automobile storage batteries when AC power is not available.

Analysis of cartridges is done using a laboratory GC. A special interface unit is normally required to obtain reproducible results. A GC Thermal Desorption Unit (Nutech Model 320) or a custom designed apparatus of individual choosing serves this purpose.

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[131] Operating Manual: Model 221-1A, AC/DC Sampler for Remote Sample Collecton Using Wet Chemical Collectors and Gas Chromatography Cartridges. The Nutech Corporation, Research Triangle Park, North Carolina.

Specifications [131]

DIMENSIONS:	39.4 cm (15.15 in.) wide, 36.8 cm (14.5 in.) high, 27.9 cm (11 in.) deep.
WEIGHT:	15.9 Kg (35 lb).
POWER:	110 V, 60 Hz and/or 12 V DC. DC current varies with flow. 221-1A20 draws 2.0 - 2.5 amps, 221-1A14 draws 2.0 - 3.5 amps. Built-in battery charger. Recharging time approximately equals running time.
GAS FLOW:	Max. Flow--10 - 15 Lpm. Max. Vacuum--6.8 x 10^4 - 8.1 x 10^4 Pa (20-24 in. Hg). Flowmeter--0.5 - 10 Lpm. Dry Gas Meter--280 m^3 (10,000 cu ft) total readable to 2.8 x 10^{-5} m^3 (0.001 cu ft).
SAMPLE INLET:	6.4 mm (1/4 in.) Quick Connect in upper side for easy mounting of GC cartridge holder or other sampling connections. Vacuum gauge monitors pressure drop across cartridge.

Operating Procedure [131]

- The Model 221 gas sampler comes equipped with a 120 volt power cord and external battery supply leads for a 12 volt automobile storage battery which the user must supply.
- The Model 221 is ready to be put into operation.
- Figure C-7 shows the switching arrangement for AC and DC operation and the charging mode.
- For AC operation, turn on AC switch and then DC switch.
- For DC operation, connect battery terminals to battery and plug into side receptacle. Turn on DC switch to start pump. (AC switch is inoperative in this mode.)

		AC SWITCH	
		ON	OFF
DC SWITCH	ON	PUMP OPERATING FROM RECTIFIED AC POWER. ALSO SUPPLIES BATT. CHARGE	PUMP ON BATTERY. POWER.
	OFF	BATTERY CAN CHARGE	SYSTEM OFF

Figure C-7. Switching arrangement [131].

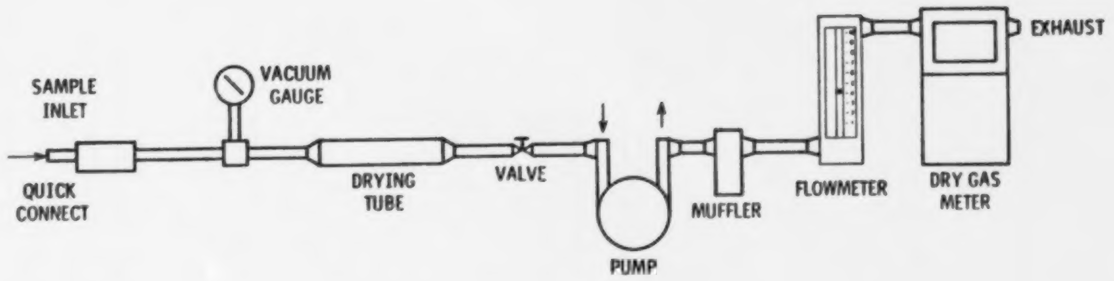

SAMPLE INLET
VACUUM GAUGE
QUICK CONNECT
DRYING TUBE
VALVE
PUMP
MUFFLER
FLOWMETER
DRY GAS METER
EXHAUST

Figure C-8. Flow diagram for Nutech Model 221 AC/DC Gas Sampler [131].

Maintenance [131]

Pump--
The pump (see Figure C-9) is a permanently lubricated, permanent magnet low battery drain, DC operated diaphragm pump.

Replacing a Diaphragm--Remove the four head screws to remove the head. Then remove the two diaphragm hold-down plate screws and replace diaphragm. To reassemble reverse the above procedure.

Replacing the Intake Valve--Remove four head screws to remove the head. Remove the valve hold-down screw and replace valve. Reverse procedure to reassemble.

Replacing the Exhaust Valve--Remove the four head screws and remove the head. Turn the head upside-down and remove the flat Phillips' head screws in the valve plate.

After the screws have been removed, turn the head over on a flat table. Introduce a slight amount of air from an air line or blow gun into the exhaust part of the head. Be careful that not too high a pressure is used [approximately 1.4 x 10^5 Pa (20 psi)]. This will blow the valve plate down on the table if the exhaust valve itself is intact. If the valve plate gasket becomes torn or mutilated through this disassembly, it should be replaced.

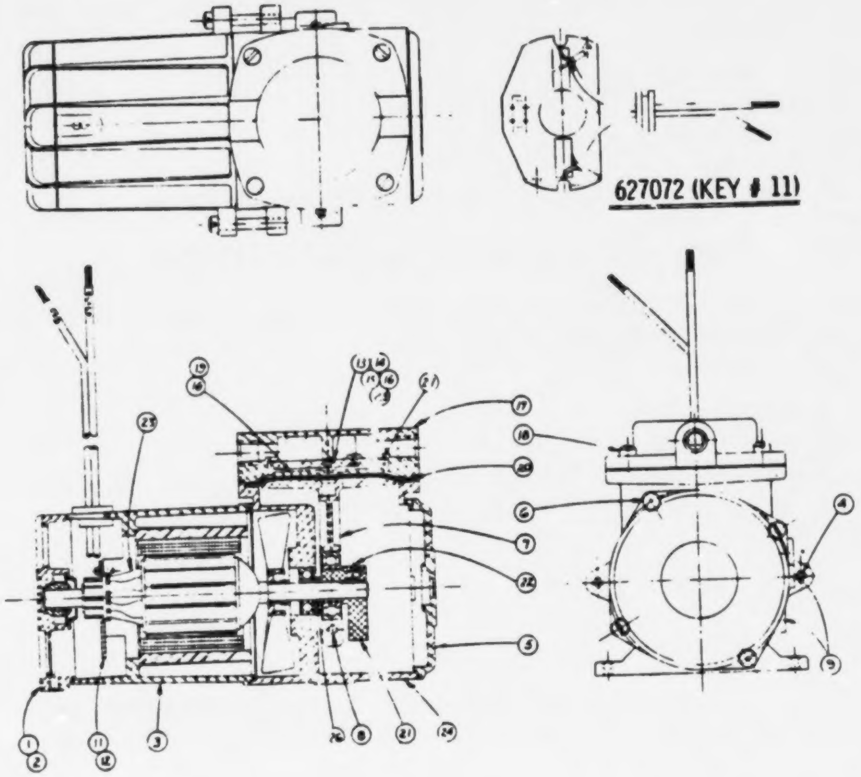
The valve on the valve plate can now be replaced by removing the valve hold-down screw and replacing the valve. In order to reassemble reverse this procedure.

Replacing the Eccentric & Bearing Assembly--Remove the two front cover screws and remove cover. With a 4.0 mm (5/32 in.) Allen wrench remove the two pipe plugs on right side of housing. Loosen the set screw in the eccentric (Key No. 22) with a 3.2 mm (1/8 in.) Allen wrench by going through the port hole in the side of the housing. Next loosen the cap screw on the lower end of the connecting rod with a 4.0 mm (5/32 in.) Allen wrench. After this has been done, the eccentric and bearing assembly (Key No. 21) can be removed. To reassemble, reverse procedure. Do not over-tighten connecting rod screw, 1.7 J (15 in.-lb) is sufficient. The eccentric screw cannot be over-tightened.

Replacing Brushes--The complete brush holder and lead wire assembly (Key No. 11) must be replaced. Remove the two and cap screws and remove end cap. Then remove two screws holding brush cord. Pull complete brush holder and rubber grommet out of housing. To replace, reverse procedure. Be sure to keep brushes inside of brush guide before placing over commutator.

Valve--
A specially designed stem point in the metering valve permits positive shut-off on a separate seat. The fine metering needle

PARTS LIST FOR PUMP



KEY	PART No.	DESCRIPTION
1	614377	MOTOR END CAP ASSEMBLY
2	623260	SCREW - M.E.C.
3	602492	MOTOR HSG & MAGNET ASSEMBLY
4	625058	SCREW - SLEEVE TO HSG
5	614372	FRONT COVER
6	625266	SCREW - FRONT COVER
7	607139	CONN. ROD
8	625114	SCREW - CONN. ROD
9	63364	FLUSH SEAL PIPE PLUG
11	627072	BRUSH & LEAD WIRE ASSEMBLY
12	625006	SCREW - BRUSH ASSEMBLY
13	617045	VALVE KEEPER
14	621102	VALVE FLAPPER
15	654129	VALVE PLATE
16	625141	SCREW - VLV. & H.D. PL.
17	660131	HEAD
18	625109	SCREW-HEAD
19	654649	DIAPH. H.D. PLATE
20	608148	DIAPHRAGM
22	625244	SET SCREW - ECC
23	608092	ARMATURE FAN & BRNG. ASSEMBLY
24	660437	HOUSING
25	625160	SCREW - FLAPPER
26	615403	SPACER
27	633439	GASKET - VLV. PLATE

Figure C-9. Parts list for pump [131].

is used only for flow control and can be shut off just like a blunt nose valve without the metering qualities.

There are 10 full turns from full close to full open, 8 of which are for fine metering.

Materials are the following:
    Body: Brass forging
    Stem: 316 stainless steel
    Packing: Teflon
    Maximum operating pressure: 2.1×10^7 Pa (3000 psi) at 21°C (70°F).
    Temperature range: -51°C (-60°F) to 230°C (450°F).

Flow characteristics of this valve are shown in Figures C-10 and C-11 for two different pumping capacities.

Flowmeter--
Range: 0 - 10 LPM
Accuracy: 5% of full scale
Calibration: The flow meter has been factory calibrated. If you wish to re-check calibration do so only with devices of certified accuracy.

Temperature Limit: 66°C (150°F)

Pressure Limit: 6.9×10^5 Pa (100 psi)

Atmosphere: Do not expose to strong chlorine atmospheres or solvents such as benzene, acetone, carbon tetrachloride, etc.

Disassembly: The flowmeter can be disassembled for cleaning by disconnecting the piping, dismounting the unit from the panel and removing the top-plug-ball stop. Remove ball by inverting the body and letting the bell fall into your hand.

Cleaning: The flow tube and body can be cleaned with pure soap and water and a soft bottle brush. Do not use benzene, acetone, carbon tetrachloride, alkaline detergents, caustic soda or liquid soaps.

Reassembly: Reinstall float, remount, connect piping and put the unit back in service.

Dry Gas Meter--
To replace front gasket, remove four mounting screws from dial cover. Install new gasket and reassemble. To replace large top mounting gasket, remove dial face cover, remove dial face assembly by removing two dial face mounting screws. Next remove 8 screws holding meter top to meter bottom; remove old gasket, clean surfaces, install new gasket and reassemble.

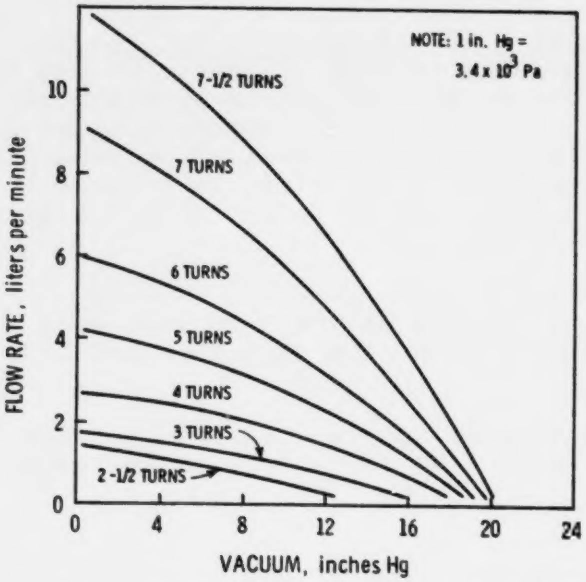


Figure C-10. Typical flow rate versus inlet pressure drop for Model 221-1A14 [131].

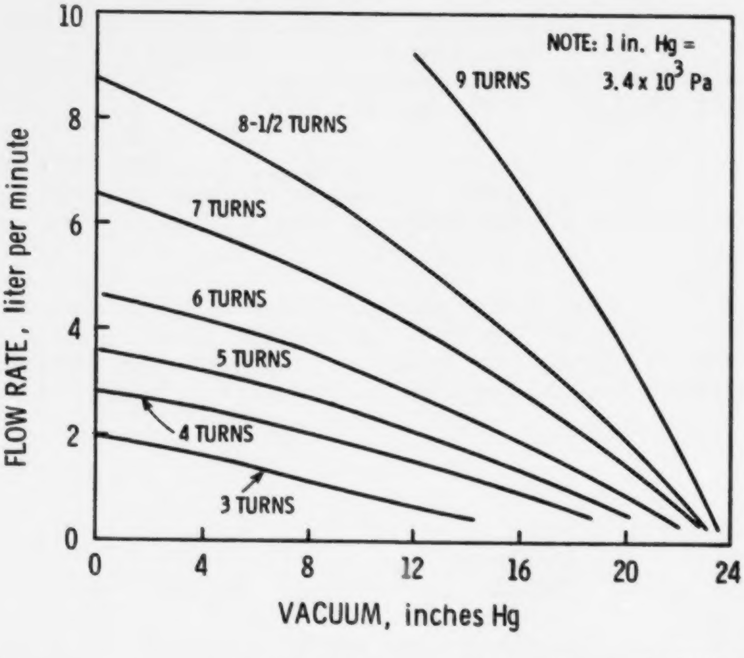


Figure C-11. Typical flow rate versus inlet pressure drop for Model 221-1A20 [131].

Since meter body is made of aluminum, use force sparingly to tighten pipe nipple.

Vacuum Gauge [0 to 1.02 x 10^5 Pa (0 to 30 in. Hg)]--
The Bourdon tube type gauge is made of brass. A pin hole permits the sensor element to come to equilibrium with the gas in the sample line. If this pin hole should become plugged making the gauge inoperative, the gauge may be removed by removing two screws in the rear of the panel. A small wire can be used to clear the hole. Care should be taken not to tamper with the sensor mechanism and alter the calibration.

Drying tube--
Make sure end caps are all the way on. To make ends more secure wrap each end once with pipe dope tape before replacing end caps.

When installing drying agent, place glass wool in one end, fill with drying agent, finish with glass wool on the other end and secure end caps.

Power Supply--
Requires 120 V, 60 Hz input; 12 V DC output.

Input and output connections are shown in Figure C-12 with the numbers corresponding to the barrier strip on the power supply with terminal one toward the front of the sampler console. The DC output supplies the pump motor when the AC and DC switches are in the ON positions; the DC output charges an external battery with the AC switch in the ON position and the DC switch in the OFF position. The sampler can be operated from an external 12 V DC source with the DC switch in the ON position.

Be careful not to short the battery terminal connector leads when AC power is in ON position. DC power connection should always be made or broken by unplugging from the cabinet.

Battery Connections--
Battery connections are made by plugging the plug on the battery leads into the battery lead receptacle on the side of the sampler and connecting the clips to the + and - poles of the battery. Be careful to observe polarity--red is positive; black is negative.

Parts List [131]--

221-001	Base
221-002	Cabinet
221-003	Panel
221-004	Cabinet Cover
221-005	Battery Charger

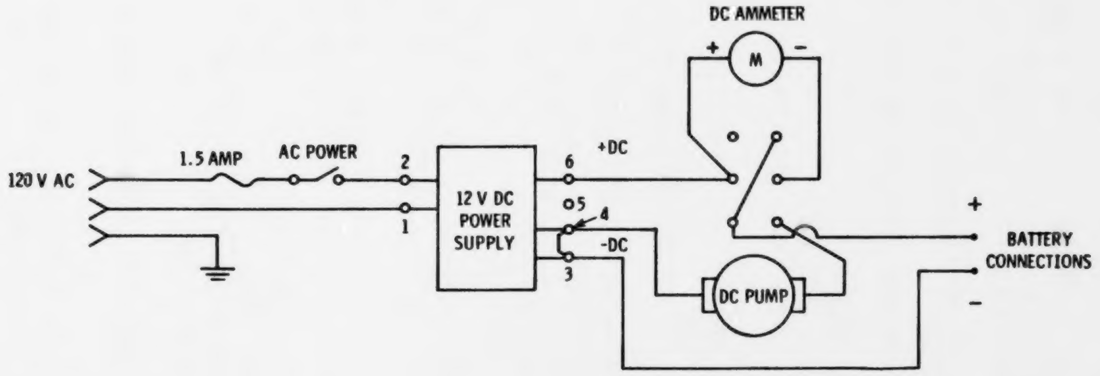

DC AMMETER
+
M
-
120 V AC
1.5 AMP
AC POWER
2
1
12 V DC POWER SUPPLY
6
+DC
o5
4
-DC
3
DC PUMP
+
BATTERY CONNECTIONS
-

Figure C-12. Wiring block diagram for Nutech Model 221 AC/DC Gas Sampler [131].

221-006	6 Terminal Barrier Strip
221-007	AC Plug
221-008	DC Socket
221-009	DC Plug & Battery Leads
221-010	Fuse (1 1/2 amp)
221-012	AC Switch (SPST or SPDT)
221-013	DC Switch (DPDT)
221-014	Ammeter
221-015	6.40 mm (1/4 in.) Quick Connect
221-016	6.4 mm (1/4 in.) SS Elbow
221-017	Mtg. Bracket for SS Elbow
221-018	"T"
221-019	3.2 mm (1/8 in. NPT to 4.8 mm (3/16 in.) Hose Connector
221-020	Vacuum Gauge [0-1.02 x 10^5 Pa (0-30 in. Hg.)
221-021	Drying Tube
221-022	Metering Valve
221-023	3.2 mm (1/8 in.) NPT Street Elbow
221-024	Muffler
221-025	3.2 mm (1/8 in.) to 6.4 mm (1/4 in.) Male Union
221-026	6.4 mm (1/4 in.) NPT to 4.8 mm (3/16 in) Hose Connector
221-027	Flow Meter (0 - 10 LPM)
221-028	Dry Gas Meter
221-029	12.7 mm (1/2 in.) to 6.4 mm (1/4 in.) NPT Reducing Bushing
221-030	3-Conductor Power Cord
221-031	4.8 mm (3/16 in.) ID Tubing
221-032	Pump (Specify Size 35.6 cm (14) or 50.8 cm (20 in.) Brackets)

To order replacement parts or to obtain further information about the Nutech Air Sampler write or telephone:

Nutech Corporation
P.O. Box 12425
Research Triangle Park, N.C. 27709
(919) 682-0402

Calibration of the Nutech Air Sampler for the Ambient Air Collection System

Prior to using the Nutech Air Sampler as part of the ambient air collection system for obtaining air samples, certain parts of the Nutech Air Sampler should be properly calibrated. The most important variable to determine during sample collection is the total volume of the sample collected. This is true because this volume is used in combination with the amounts of various compounds analyzed in the collected samples to determine the concentrations of the compounds in the original air samples. Therefore, the dry gas meter of the Nutech Air Sampler should be properly calibrated prior to each sampling program to allow an easy and accurate determination of the total sample volume for each sample. Calibration of the dry gas meter can be performed using a calibrated wet test meter by standard procedures. For additional certainty, the flow meter (rotameter) of the Nutech Air Sampler should also be calibrated prior to each sampling program (and rechecked immediately before and after each sample is collected). This can be done by using a calibrated mass flow meter or bubble meter [132]. This rotameter can be used during sampling to monitor the flow rate through the ambient air collection system. The average or integrated flow rate can then be multiplied by the sampling time to yield a total sample volume which can be compared to the sample volume determined by the dry gas meter.

Design and Preparation of the Sorbent Tube Tray

This part of this manual describes the preparation of the sorbent tube tray which is used to contain the replaceable sorbent cartridges that collect and concentrate organic vapors from an air stream passing through them. The preparation, cleaning, and conditioning of these replaceable sorbent cartridges was described in a previous section of this manual. At the end of that section, the sorbent tubes, consisting of three types (Tenax-GC, Porapak R, and Ambersorb XE-340), were ready to be used for sample collection. Through cleaning and conditioning their background levels had been reduced to a minimum and this minimal background level maintained by storing the tubes capped with metal fittings and o-rings inside a culture tube with a Teflon-lined screw-top cap. The hardware needed for the storage of each sorbent tube is described in Table C-2 and the use of these materials for tube storage is demonstrated by Figure C-13. For sample collection, four sorbent tubes of specific types will be connected in series within a special tray, such that the collected air sample first passes through a Tenax sorbent tube, then through a Porapak R sorbent tube, then through an Ambersorb XE-340 sorbent tube, and finally through a second, backup, Ambersorb XE-340 sorbent tube. With these sorbent tubes connected in series in this order, the highest molecular weight compounds will be collected on the Tenax tube, which has the greatest ability of the three sorbents to desorb such compounds. Any intermediate or low molecular weight compounds which "break through" the Tenax tube are then collected by the Porapak R sorbent tube. Very volatile, low molecular weight compounds will "break through" the Porapak R tube also and pass into the first Ambersorb tube which, of the three sorbents, has the greatest ability to retain such compounds. Hopefully, this combination of

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[132] "Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. II". U.S. Environmental Protection Agency, May 1977.

TABLE C-2. HARDWARE MATERIALS REQUIRED FOR STORAGE OF EACH SORBENT TUBE

Item	Material	Size-brand	Quantity
Nut	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
Front ferrule	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
Cap	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
O-ring	Viton	~6.4 mm (~1/4 in.) O.D.	Two
Culture tube	Glass	20 cm long x 2.5 cm diameter-Pyrex, Kimax or equivalent	One
Culture tube screw-top cap	Plastic with teflon liner	for 2.5 cm diameter culture tube	One

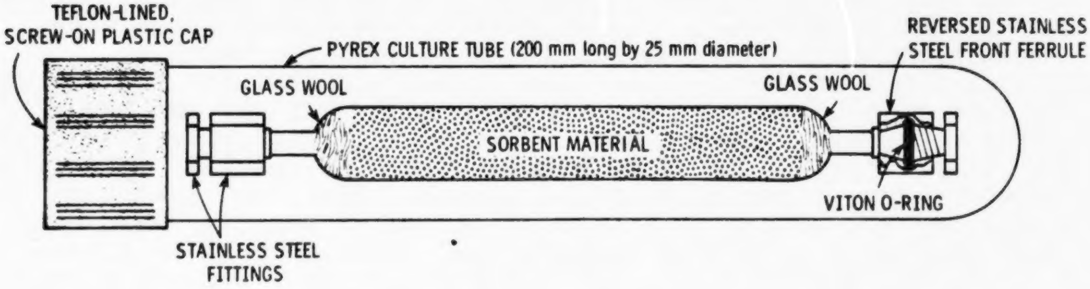
TEFLON-LINED, SCREW-ON PLASTIC CAP
PYREX CULTURE TUBE (200 mm long by 25 mm diameter)
REVERSED STAINLESS STEEL FRONT FERRULE
GLASS WOOL
GLASS WOOL
SORBENT MATERIAL
VITON O-RING
STAINLESS STEEL FITTINGS

Figure C-13. Storage of a sorbent tube.

three tubes will quantitatively collect all compounds of interest to this project, however, some of the very volatile, low molecular weight compounds may "break through" the first Ambersorb tube and pass into the second, backup Ambersorb tube. This backup tube serves to check the ability of the first three tubes to retain the compounds of interest to this project. The quantities of compounds on one or more of the first three sorbent tubes, and not found on the backup tube, should be summed to obtain the total amounts collected. These amounts can then be divided by the sample volume collected to determine the approximate original concentrations of the compounds found in ambient air. For compounds found on the backup sorbent tube as well as one or more of the first three sorbent tubes, their summed quantities should be considered to represent the minimum amounts of these compounds present in the sampled air. When dividing these quantities by the sample volume collected, the concentrations of these compounds in ambient air should be reported as greater than or equal to the values obtained.

In some instances, such as if a number of samples are collected simultaneously, the analysis of one or two Ambersorb backup tubes may suffice to ascertain which, if any, compounds have "broken through". It may then not be necessary or desirable to analyze the rest of the Ambersorb backup tubes collected. Where such a situation is anticipated, using backup tubes with each sample collected may not be desired. Therefore, the backup tubes can be replaced in some of the sorbent tube trays by a piece of stainless steel tubing (6 mm O.D., ~14 mm long). If any question exists about whether or not backup tubes should be used on certain samples, it would probably be advisable to collect the backup samples and later decide whether they should be analyzed.

Figure C-14 gives the dimensions of the aluminum box to be used as a tray for containing the sorbent tubes. It also shows the locations and sizes of holes to be drilled for attaching the tube retaining clips, the tray cover, and the 6.4 mm (1/4 in) stainless steel bulkhead unions. The rest of the hardware necessary for use within the sorbent tube tray are listed in Table C-3. For cleaning, the aluminum box and retaining chips should be rinsed with tap water and dried. The rest of the hardware materials for the sorbent tube tray should be prepared according to the procedures given previously for the cleaning of hardware materials for sorbent tube storage. After cleaning the sorbent tube tray and fittings, three stainless steel/teflon connectors, as depicted in Figure C-15, should be assembled in the laboratory using appropriate care such as by wearing protective gloves to prevent contamination from handling. The stainless steel/teflon connectors should then be placed within the tube tray and the cover placed on the tray to assure that all necessary parts are readily available for the "loading" of this tray with sorbent tubes in the field.

TABLE C-3. HARDWARE REQUIREMENTS FOR EACH TUBE TRAY

Item	Material	Size (brand)	Quantity
Tray with cover	Aluminum	20 cm (8 in.) x 11 cm x (4 1/2 in.) x 4 cm (1 1/2 in.)	One
Bulkhead union	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Two
Reducing union	Stainless steel	6.4 mm (1/4 in.) to 3.2 mm (1/8" in.)-Swagelok	Six
Nut	Stainless steel	3.2 mm (1/8 in.)-Swagelok	Six
Front ferrule	Stainless steel	3.2 mm (1/8 in.)-Swagelok	Six
Back ferrule	Stainless steel	3.2 mm (1/8 in.)-Swagelok	Six
Plug	Stainless steel	6.4 mm (1/4 in.)-Swagelok	Ten
Tubing	Teflon	57 mm (2 1/4 in.) to 64 mm (2 1/2 in.) long, 5.1 mm (1/5 in.) O.D., 1.6 mm (1/16 in.) I.D.	Three
Clips	(Metal)	- for 12 mm O.D. tubes	Eight
Screws	(Metal)	- for tray cover - for retaining clips	Four Eight

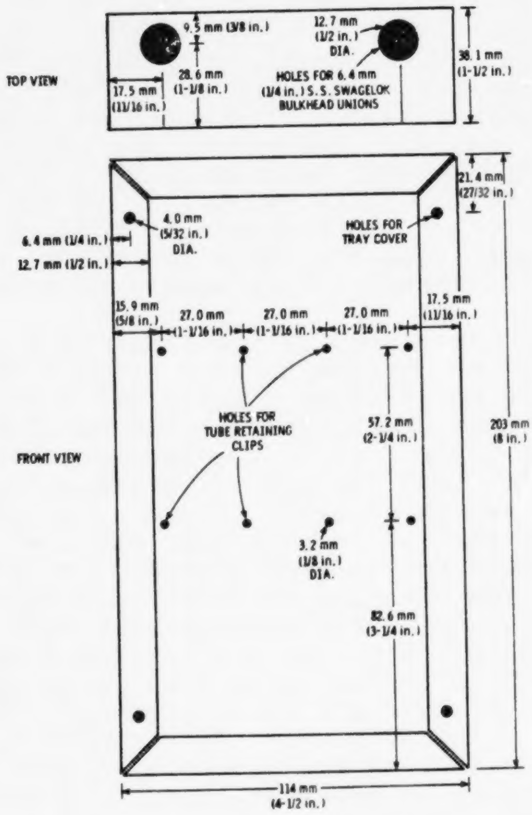
TOP VIEW
9.5 mm (3/8 in.)
12.7 mm (1/2 in.) DIA.
28.6 mm (1-1/8 in.)
HOLES FOR 6.4 mm (1/4 in.) S.S. SWAGELOK BULKHEAD UNIONS
17.5 mm (11/16 in.)
38.1 mm (1-1/2 in.)
21.4 mm (27/32 in.)
4.0 mm (5/32 in.) DIA.
HOLES FOR TRAY COVER
6.4 mm (1/4 in.)
12.7 mm (1/2 in.)
15.9 mm (5/8 in.)
27.0 mm (1-1/16 in.)
27.0 mm (1-1/16 in.)
27.0 mm (1-1/16 in.)
17.5 mm (11/16 in.)
HOLES FOR TUBE RETAINING CLIPS
57.2 mm (2-1/4 in.)
203 mm (8 in.)
FRONT VIEW
3.2 mm (1/8 in.) DIA.
82.6 mm (3-1/4 in.)
114 mm (4-1/2 in.)

Figure C-14. Dimensions of tube tray, and locations and sizes of drilled holes.

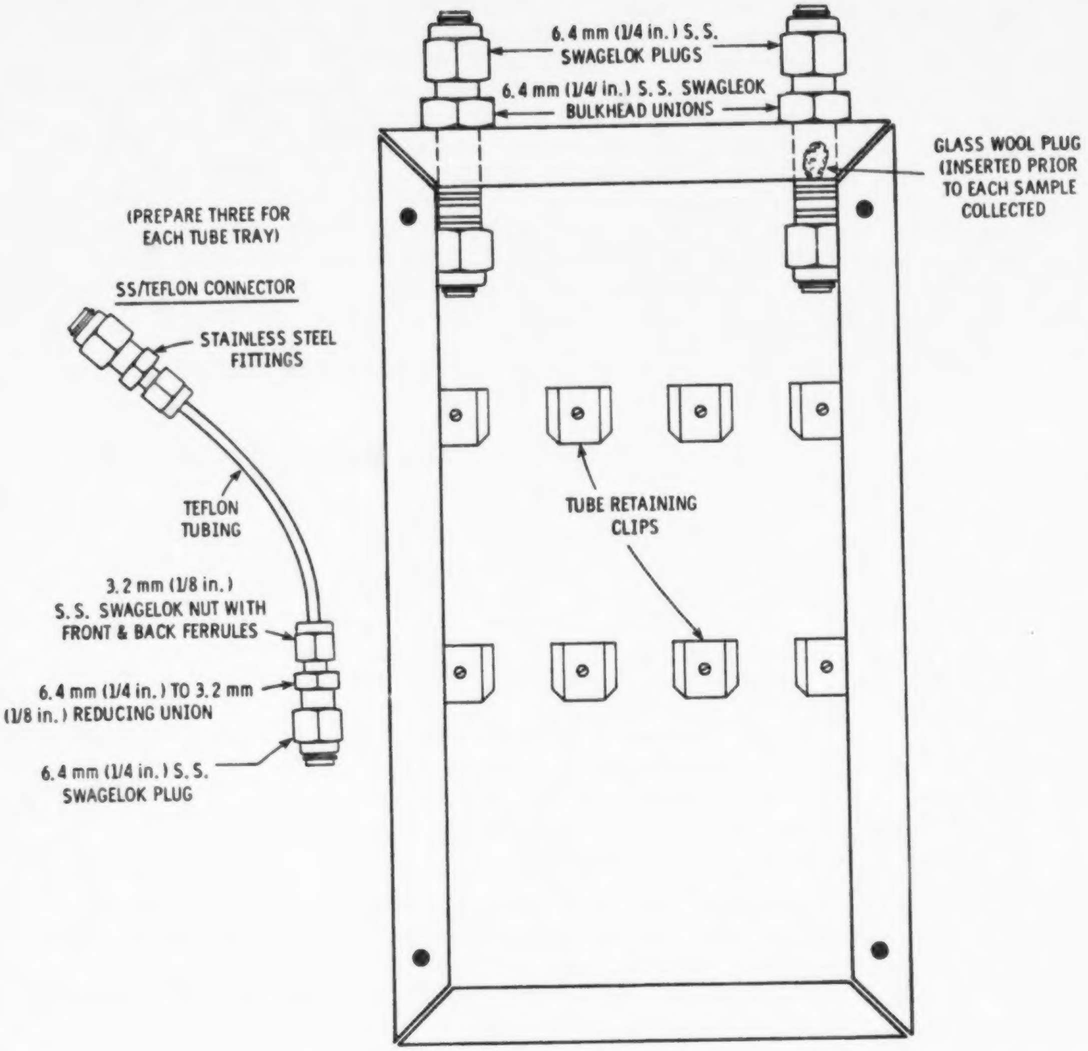
6.4 mm (1/4 in.) S.S. SWAGELOK PLUGS
6.4 mm (1/4/ in.) S.S. SWAGLEOK BULKHEAD UNIONS
GLASS WOOL PLUG (INSERTED PRIOR TO EACH SAMPLE COLLECTED
(PREPARE THREE FOR EACH TUBE TRAY)
SS/TEFLON CONNECTOR
STAINLESS STEEL FITTINGS
TEFLON TUBING
TUBE RETAINING CLIPS
3.2 mm (1/8 in.) S.S. SWAGELOK NUT WITH FRONT & BACK FERRULES
6.4 mm (1/4 in.) TO 3.2 mm (1/8 in.) REDUCING UNION
6.4 mm (1/4 in.) S.S. SWAGELOK PLUG

Figure C-15. Tube tray with all hardware assembled.

Step by step instructions for the "loading" of the tube tray with four sorbent tubes are given in Figures C-16 through C-27. It should be remembered that sorbent tubes quickly adsorb vapors from the atmosphere when they are opened, which introduces an error to the quantitation of compounds collected. Therefore, the tubes should be assembled quickly and, as shown by the figures, caps and plugs should remain in position until a connection is to be made at that position. Furthermore, once a connection is made, it should immediately be tightened with wrenches to assure a good seal. To prevent the introduction of contamination from handling the sorbent tubes, they should be assembled while wearing protective latex gloves. In addition, the ends of the sorbent tubes (i.e., at the metal fittings) should not be touched or otherwise disturbed, because these ends will later be exposed to the analytical system during sorbent tube desorption. After the sorbent tube tray is "loaded", it is ready to be connected to the Nutech Air Sampler for sample collection. Since the sorbent tubes are not as well protected from contamination within the tube tray as they are when stored, a sample should be collected with the tube tray within a few hours after being loaded.

Calibration and Operation of the Ambient Air Collection System

Before the ambient air collection system is used for sample collections, several tasks should be performed. One task is to prepare a pump/tray connector such as depicted in Figure C-28. This hardware should be cleaned by the procedures described previously for cleaning hardware materials for sample tube storage. This connector may be placed in the tube tray of the ambient air collection system, along with the stainless steel/teflon sorbent tube connectors, for transportation into the field. Also, a second, unattached tube tray should be "loaded" with four sorbent tubes (not necessarily freshly conditioned) in the manner described in the previous section. This tray will be used for measuring the flow rate of the Nutech Air Sampler prior to sample collection. The "calibration" tube tray may be transported into the field while "loaded", since some contamination of the tubes is unimportant as they will not be analyzed. In addition, the dry gas meter and rotameter of the Nutech air samples should be calibrated prior to a field sampling trip as previously described. Finally, any solutions to be used for spiking the samples collected should be prepared in the laboratory prior to field sampling.

When going into the field to collect ambient air samples, at least the items listed below should be taken.

1) Ambient Air Collection System with Nutech Air Sampler, tube tray, and all necessary connectors.

2) Power cord for the Nutech Air Sampler and a long extension cord.

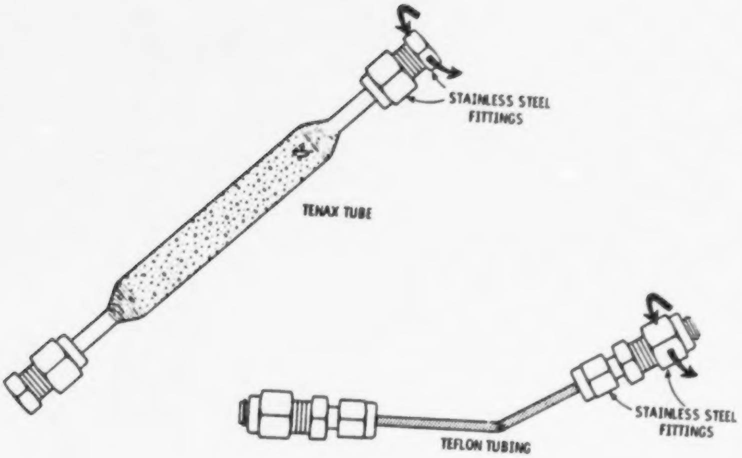
STAINLESS STEEL FITTINGS
TENAX TUBE
STAINLESS STEEL FITTINGS
TEFLON TUBING

Figure C-16. Remove cap from numbered end of a Tenax tube, and plug from one end of a stainless steel/ teflon connector.

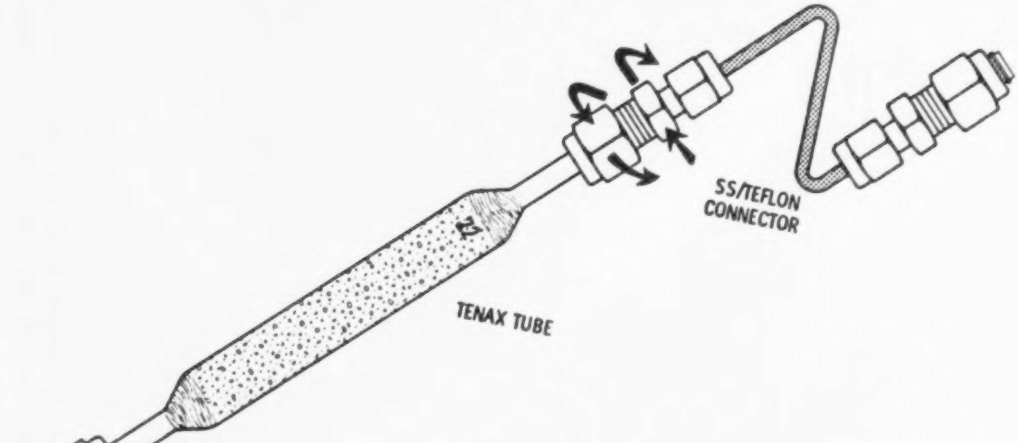
SS/TEFLON CONNECTOR
22
TENAX TUBE

Figure C-17. Attach the Tenax tube to the opened end of the stainless steel/teflon connector. Tighten with wrenches.

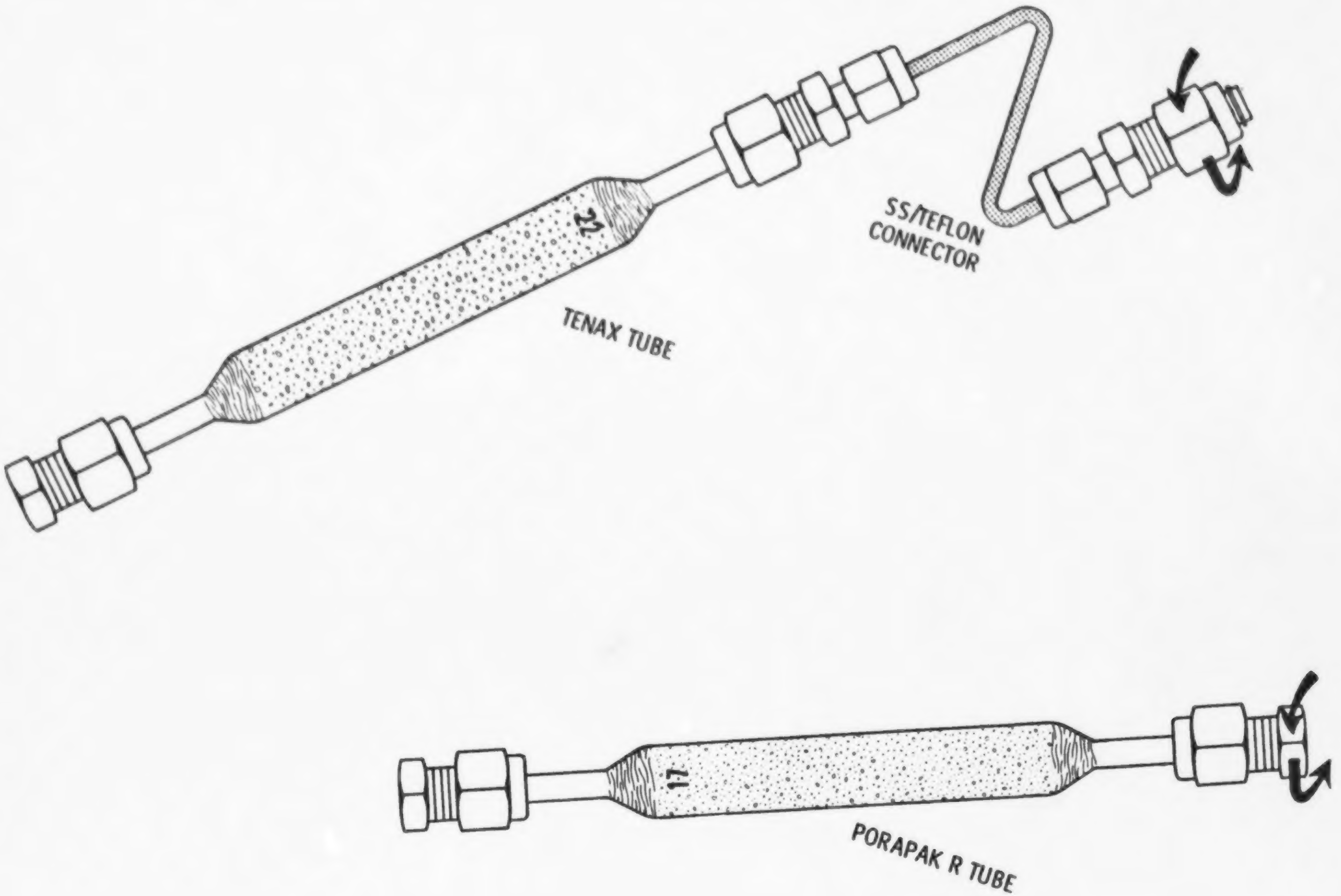
SS/TEFLON CONNECTOR
22
TENAX TUBE
17
PORAPAK R TUBE

Figure C-18. Remove plug from other end of stainless steel/teflon connector and the cap from the non-numbered end of a Porapak R tube.

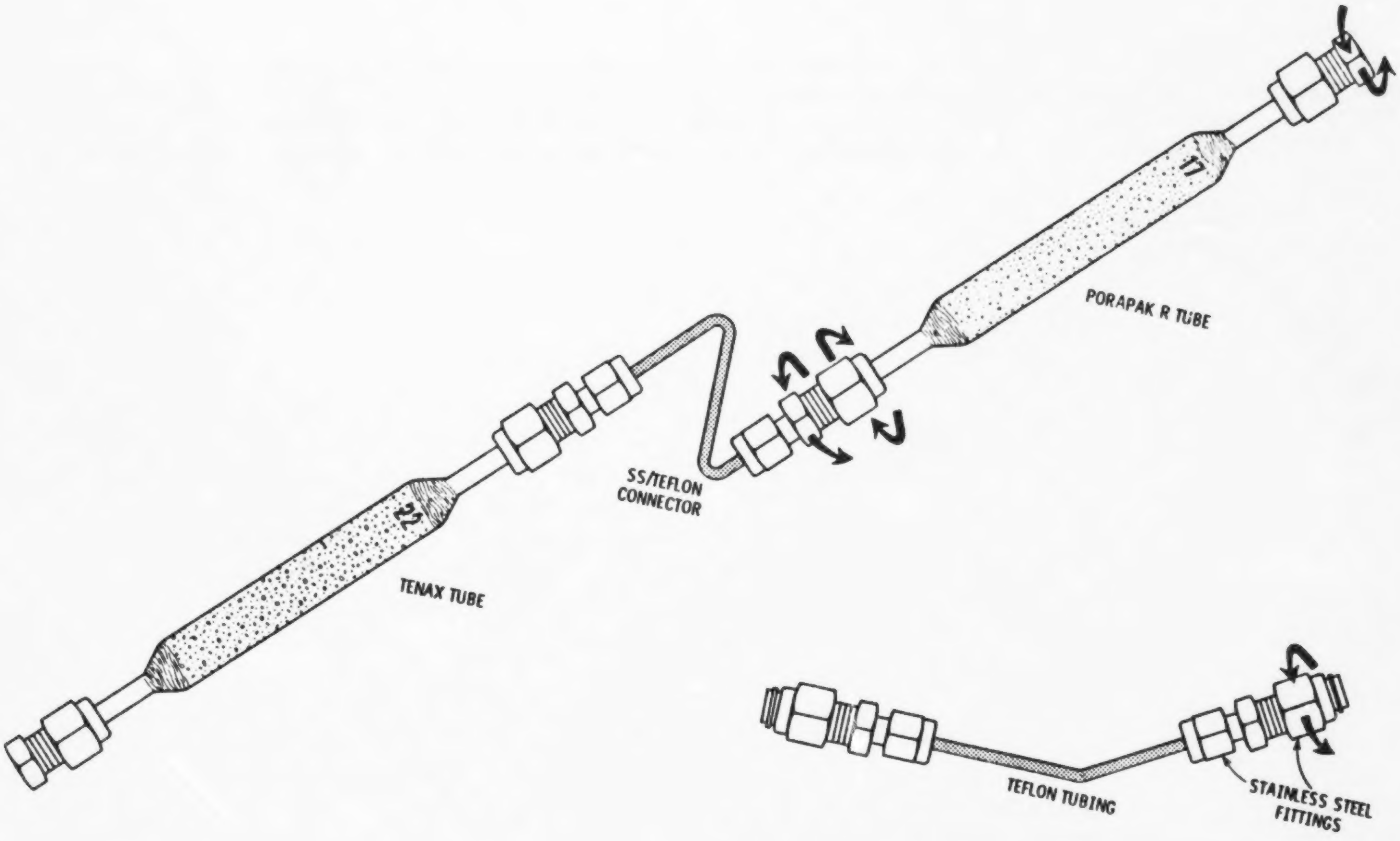
17
PORAPAK R TUBE
SS/TEFLON CONNECTOR
22
TENAX TUBE
TEFLON TUBING
STAINLESS STEEL FITTINGS

Figure C-19. Attach the Porapak R tube to the remaining end of the first stainless connector. Tighten with wrenches. Then remove cap from the other end of the Porapak R tube and a plug from one end of a second stainless steel/teflon connector.

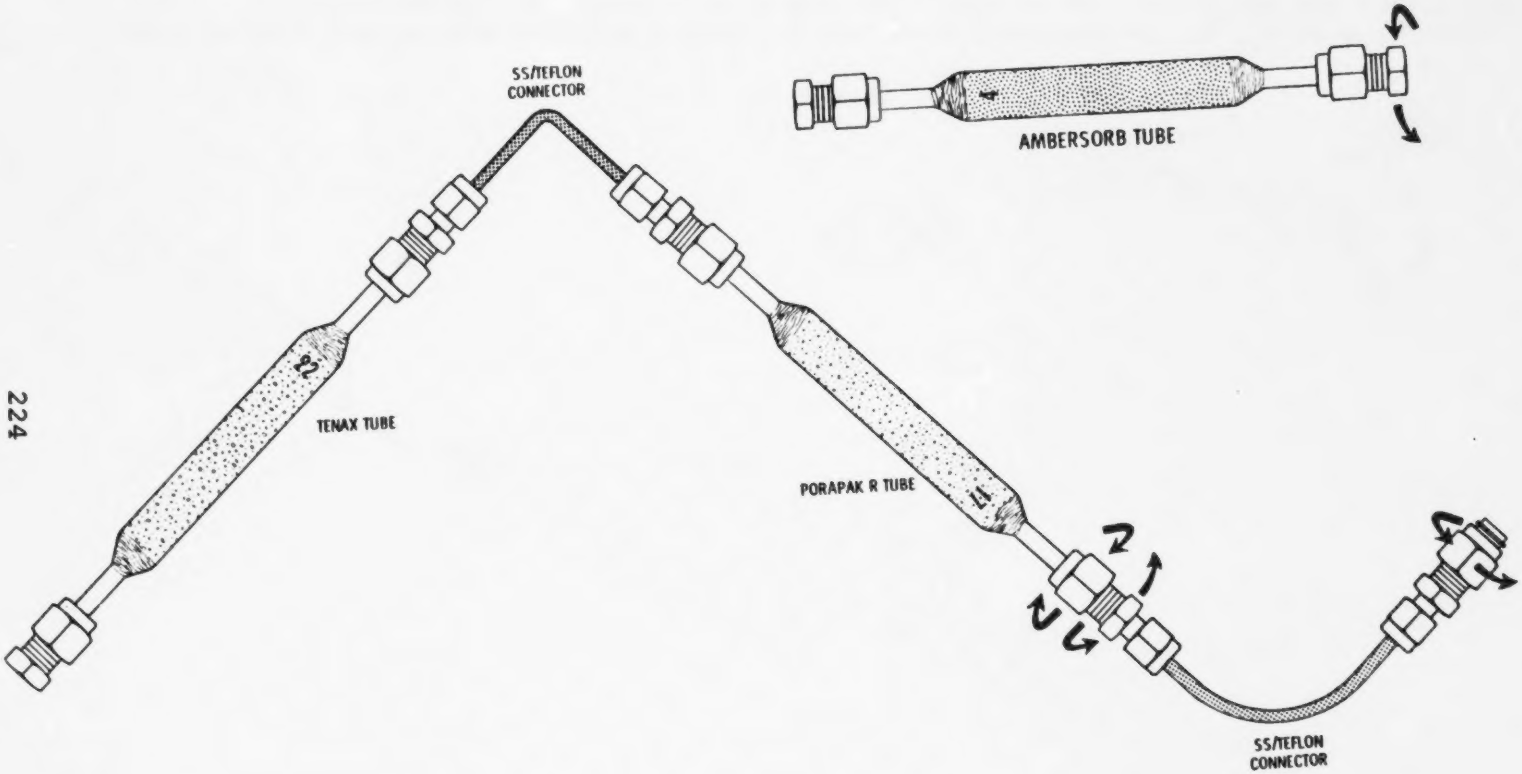
SS/TEFLON CONNECTOR
AMBERSORB TUBE
4
82
TENAX TUBE
PORAPAK R TUBE
17
SS/TEFLON CONNECTOR

Figure C-20. Attach the Porapak R tube to the opened end of the second stainless steel/teflon connector. Tighten with wrenches. Then remove the plug from the other end of the stainless steel/teflon connector and the cap from the non-numbered end of an Ambersorb tube.

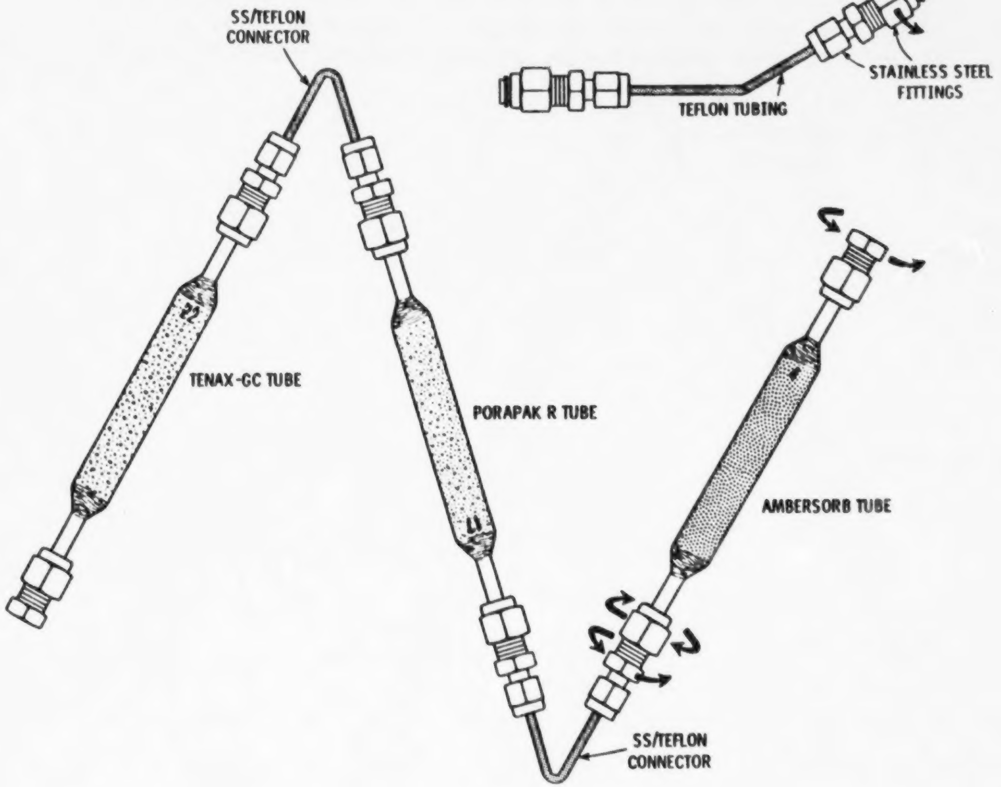
SS/TEFLON CONNECTOR
TEFLON TUBING
STAINLESS STEEL FITTINGS
22
TENAX-GC TUBE
PORAPAK R TUBE
11
AMBERSORB TUBE
SS/TEFLON CONNECTOR

Figure C-21. Attach the Ambersorb tube to the remaining end of the second stainless steel/teflon connector. Tighten with wrenches. Then remove the cap from the other end of the Ambersorb tube and a plug from one end of a third stainless steel/teflon connector.

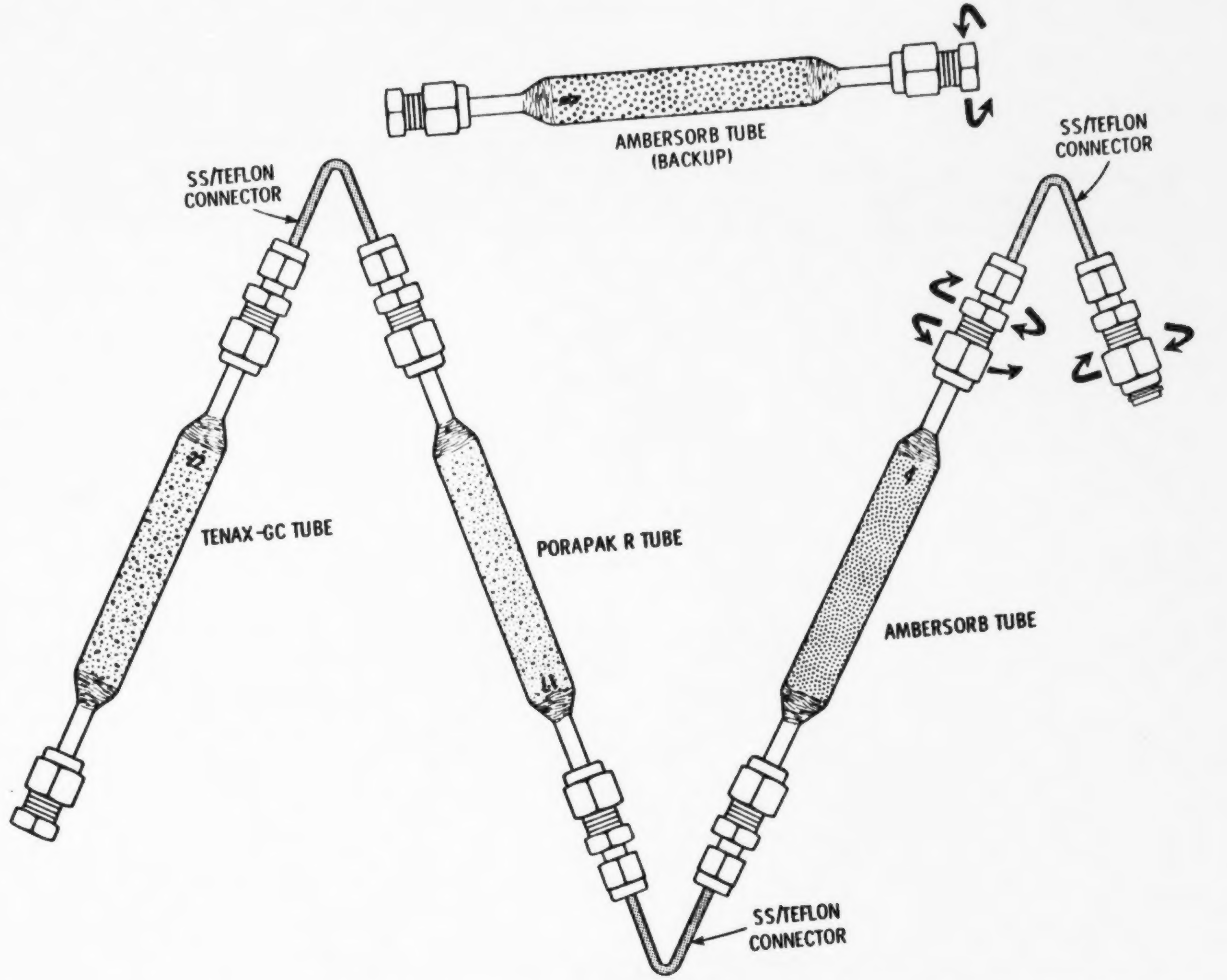
AMBERSORB TUBE
(BACKUP)
SS/TEFLON
CONNECTOR
SS/TEFLON
CONNECTOR
22
TENAX-GC TUBE
PORAPAK R TUBE
11
4
AMBERSORB TUBE
SS/TEFLON
CONNECTOR

Figure C-22. Attach the Ambersorb tube to the opened end of the third stainless steel/teflon connector. Tighten with wrenches. Then remove the plug from the other end of the third stainless steel/teflon connector and the cap from the nonnumbered end of a second Ambersorb tube (backup).

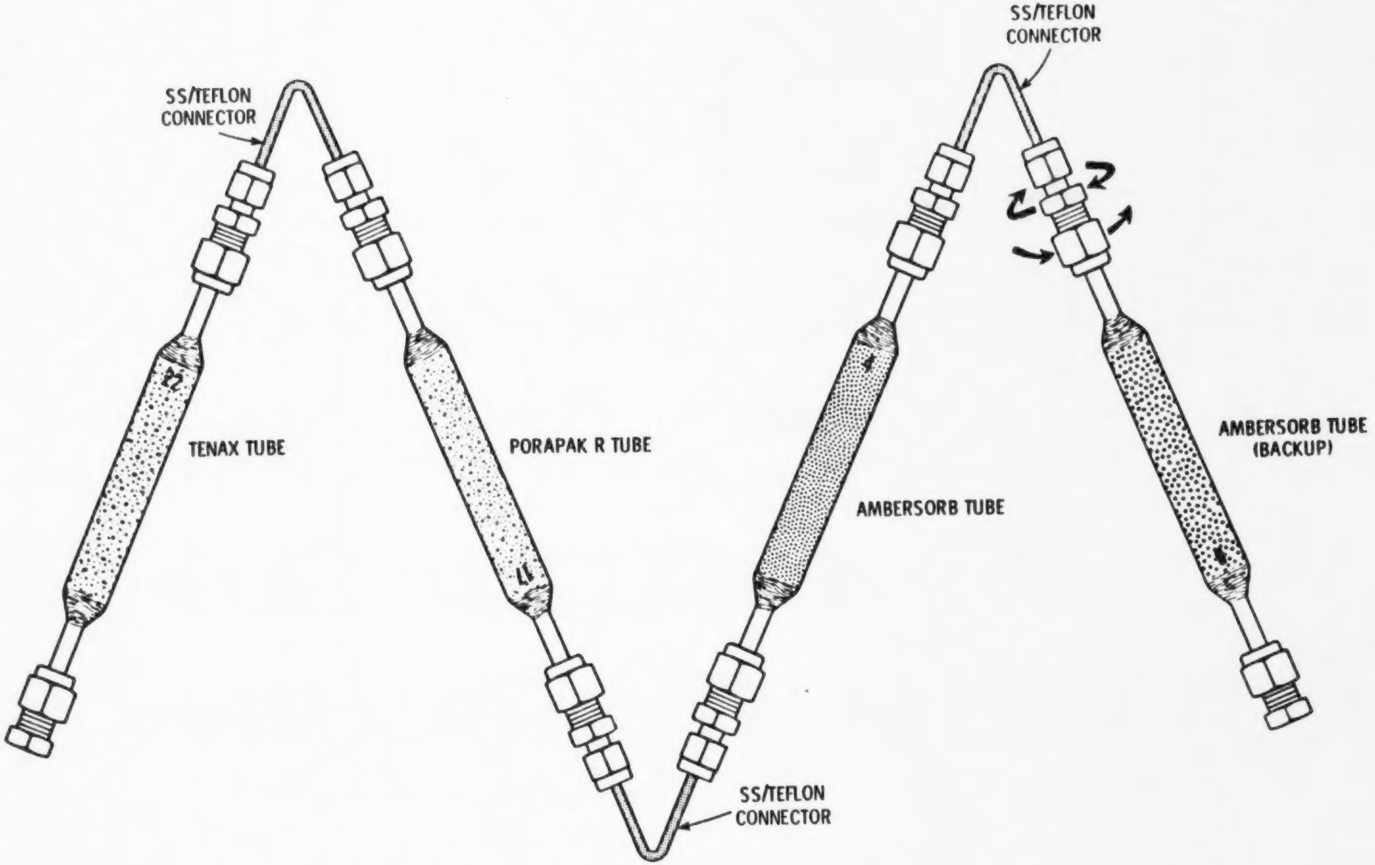
SS/TEFLON CONNECTOR
SS/TEFLON CONNECTOR
TENAX TUBE
22
PORAPAK R TUBE
17
SS/TEFLON CONNECTOR
AMBERSORB TUBE
4
AMBERSORB TUBE (BACKUP)

Figure C-23. Attach the backup Ambersorb tube to the remaining end of the third stainless steel/teflon connector. Tighten with wrenches.

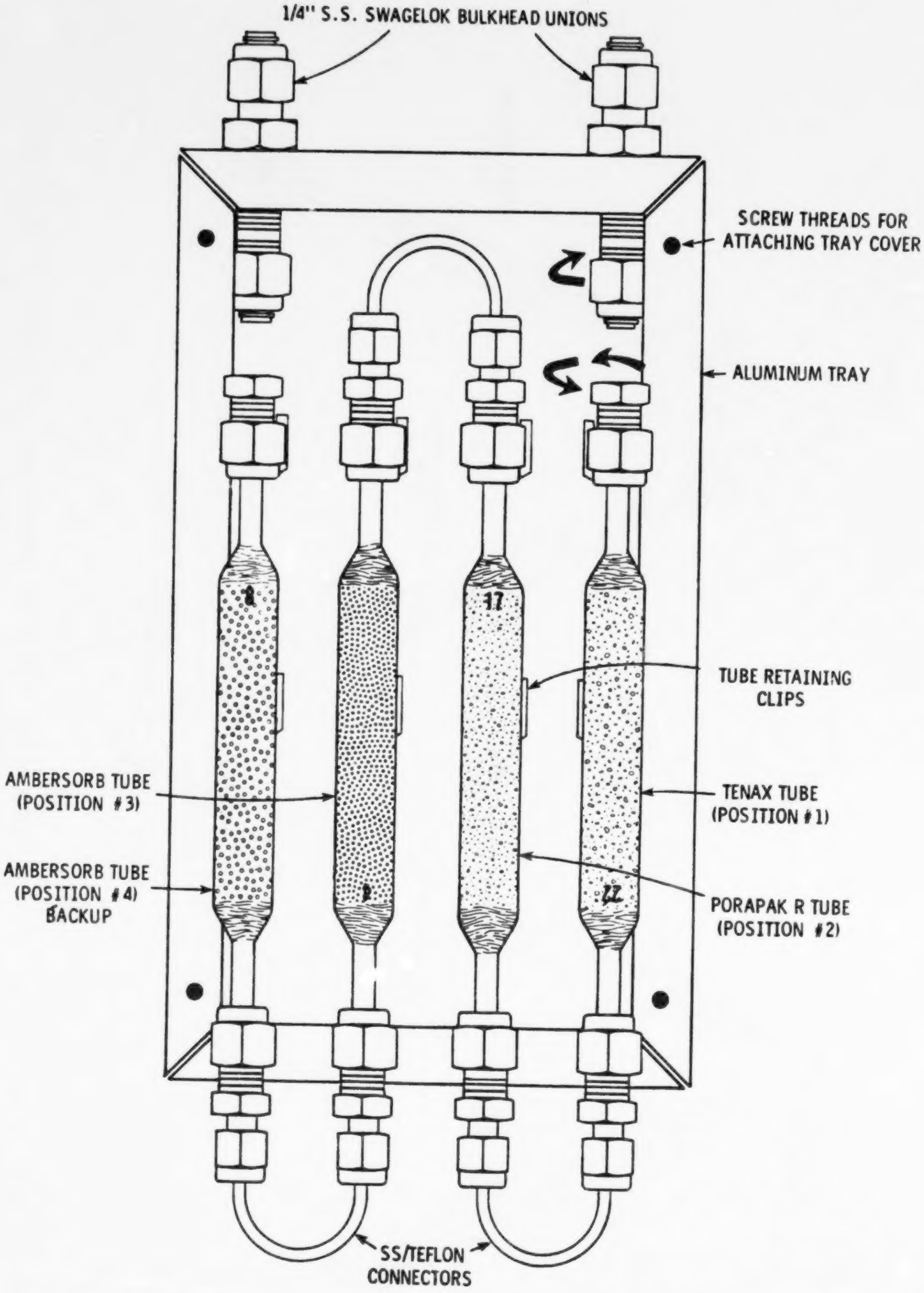
1/4" S.S. SWAGELOK BULKHEAD UNIONS
SCREW THREADS FOR ATTACHING TRAY COVER
ALUMINUM TRAY
TUBE RETAINING CLIPS
17
AMBERSORB TUBE (POSITION #3)
TENAX TUBE (POSITION #1)
AMBERSORB TUBE (POSITION #4) BACKUP
22
PORAPAK R TUBE (POSITION #2)
SS/TEFLON CONNECTORS

Figure C-24. Place series of sorbent tubes near the aluminum tube tray as shown above. Remove the plug from the inside portion of the right and bulkhead union and remove the cap from the free end of the Tenax tube.

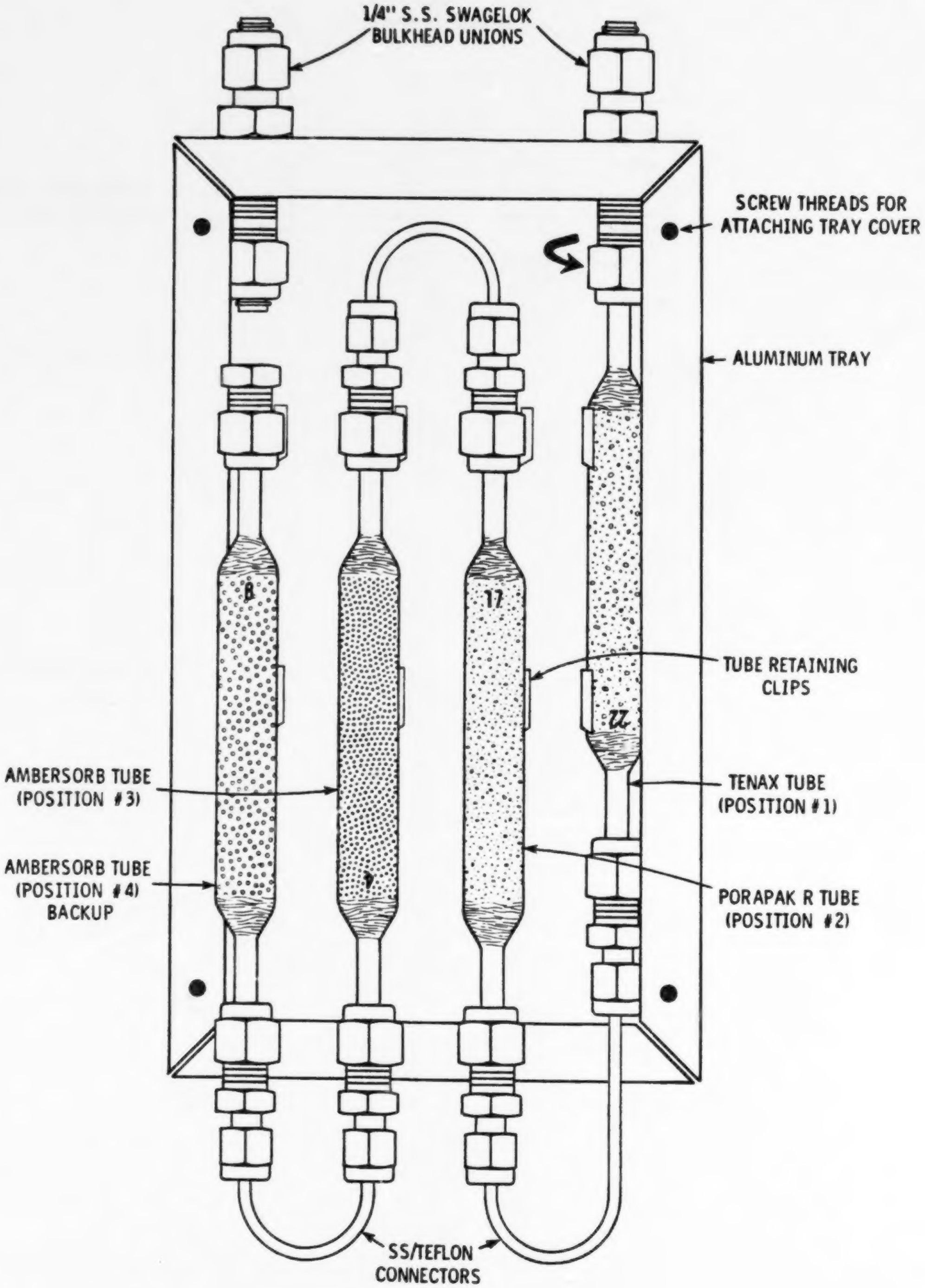
1/4" S.S. SWAGELOK BULKHEAD UNIONS
SCREW THREADS FOR ATTACHING TRAY COVER
ALUMINUM TRAY
8
17
TUBE RETAINING CLIPS
22
AMBERSORB TUBE (POSITION #3)
TENAX TUBE (POSITION #1)
AMBERSORB TUBE (POSITION #4) BACKUP
PORAPAK R TUBE (POSITION #2)
SS/TEFLON CONNECTORS

Figure C-25. Carefully slip the Tenax tube into the tube retaining clips in position #1. Slide the tube up to and attach to the opened bulkhead union. Tighten with wrench.

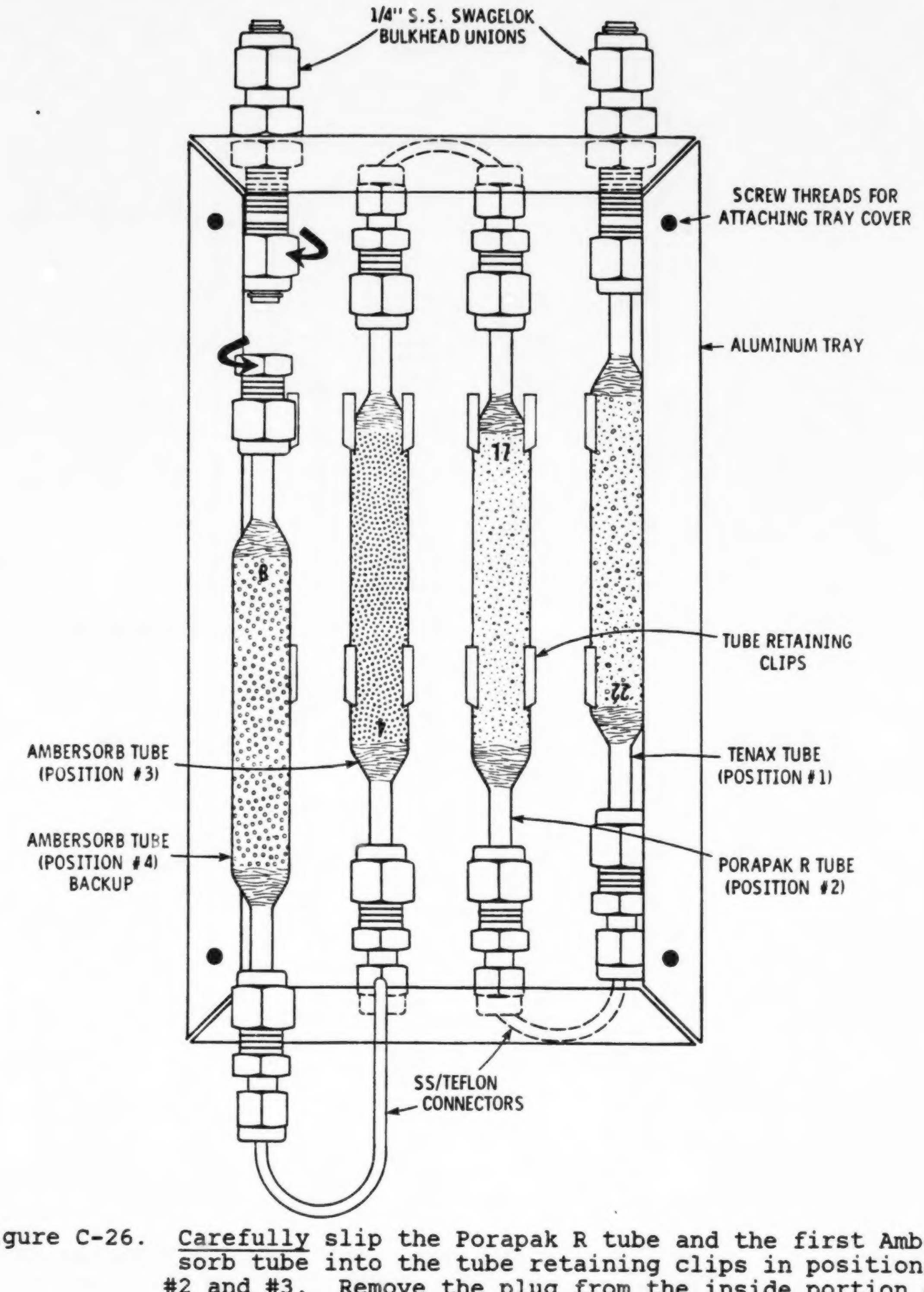
1/4" S.S. SWAGELOK BULKHEAD UNIONS
SCREW THREADS FOR ATTACHING TRAY COVER
ALUMINUM TRAY
TUBE RETAINING CLIPS
TENAX TUBE (POSITION #1)
PORAPAK R TUBE (POSITION #2)
AMBERSORB TUBE (POSITION #3)
AMBERSORB TUBE (POSITION #4) BACKUP
SS/TEFLON CONNECTORS
17
8
22

Figure C-26. Carefully slip the Porapak R tube and the first Ambersorb tube into the tube retaining clips in positions #2 and #3. Remove the plug from the inside portion of the left-hand bulkhead union and remove the cap from the free end of the second (backup) Ambersorb tube.

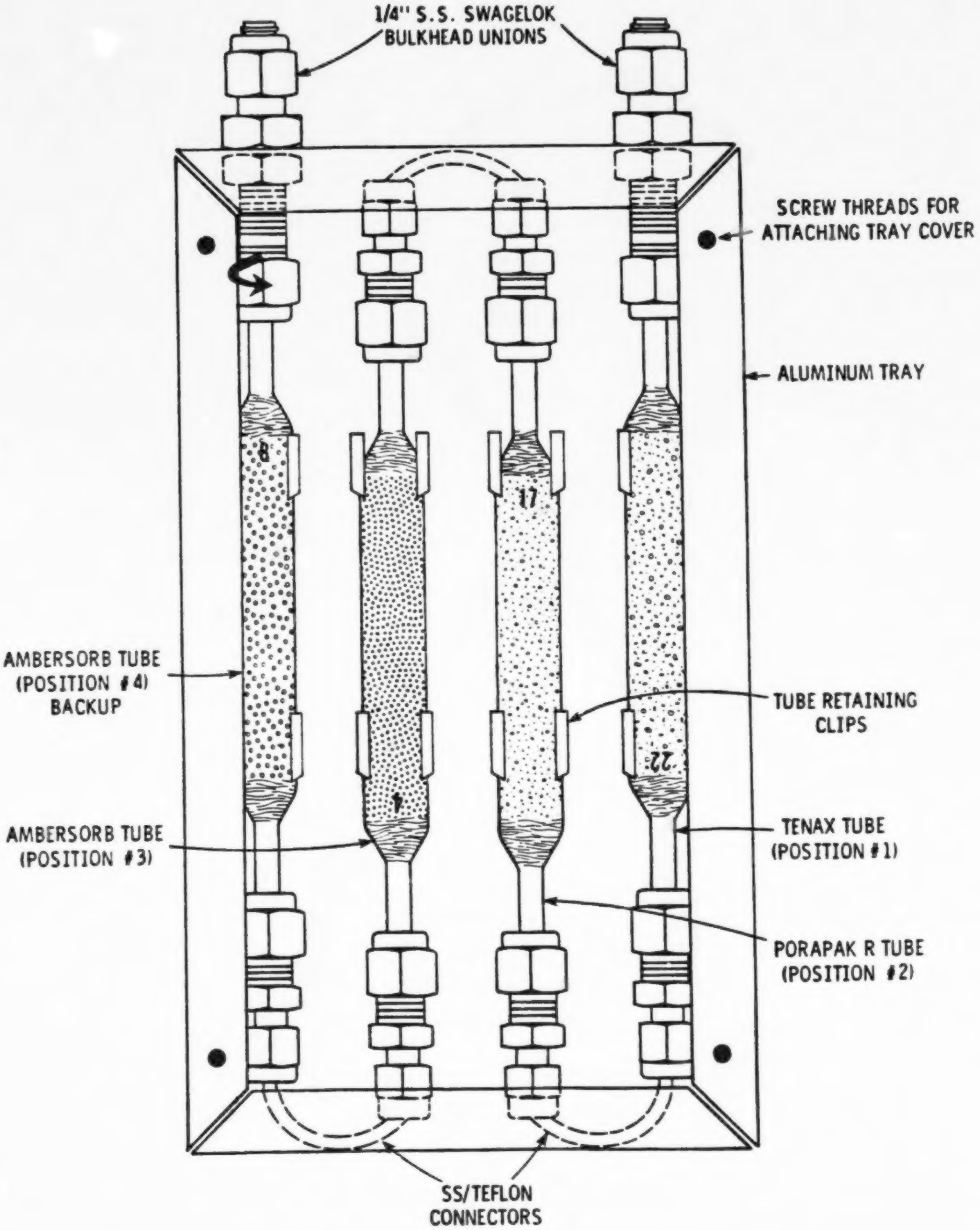
1/4" S.S. SWAGELOK BULKHEAD UNIONS
SCREW THREADS FOR ATTACHING TRAY COVER
ALUMINUM TRAY
8
17
AMBERSORB TUBE (POSITION #4) BACKUP
TUBE RETAINING CLIPS
22
AMBERSORB TUBE (POSITION #3)
TENAX TUBE (POSITION #1)
PORAPAK R TUBE (POSITION #2)
SS/TEFLON CONNECTORS

Figure C-27. Carefully slip the second Ambersorb tube (backup) into the tube retaining clips in position #4. Slide the tube up to and attach to the opened bulkhead union. Tighten with wrenches.

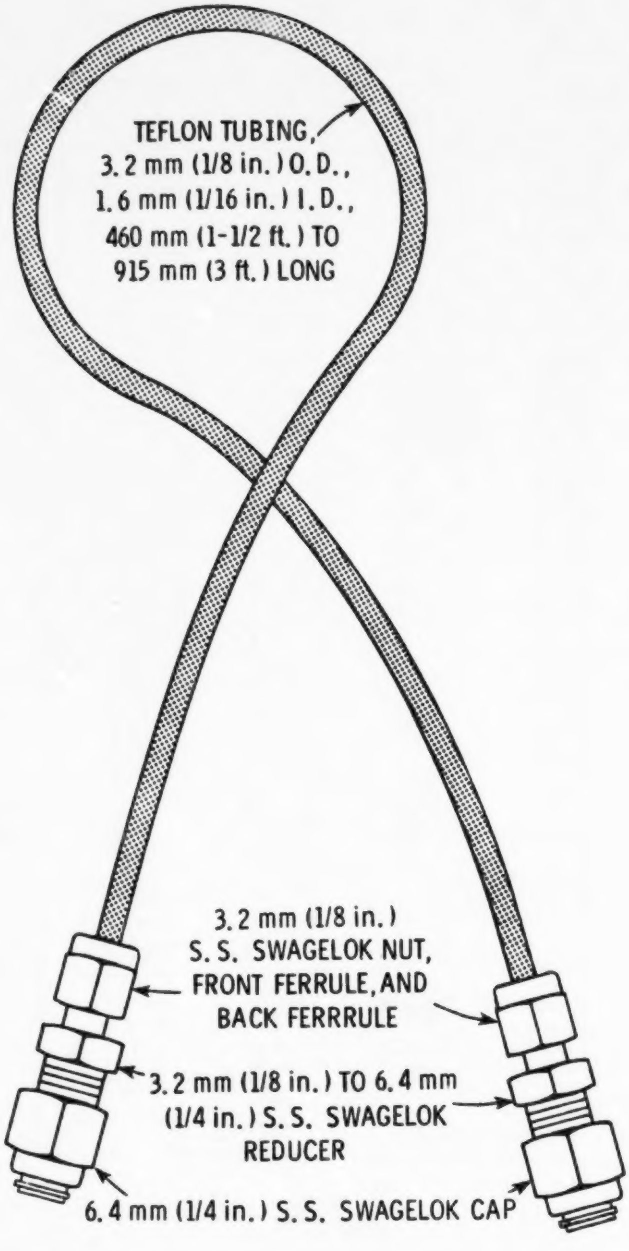
TEFLON TUBING,
3.2 mm (1/8 in.) O.D.,
1.6 mm (1/16 in.) I.D.,
460 mm (1-1/2 ft.) TO
915 mm (3 ft.) LONG
3.2 mm (1/8 in.)
S.S. SWAGELOK NUT,
FRONT FERRULE, AND
BACK FERRRULE
3.2 mm (1/8 in.) TO 6.4 mm
(1/4 in.) S.S. SWAGELOK
REDUCER
6.4 mm (1/4 in.) S.S. SWAGELOK CAP

Figure C-28. Pump/tray connector.

3) A sufficient number of stored, freshly conditioned sorbent tubes (as determined by the sampling plan, which will be discussed later).

4) A bubble meter, stop watch, and calculator for flow rate calibrations.

5) A "calibration" sorbent tube tray.

6) A stopwatch or wrist watch for measuring the sampling times.

7) Necessary tools, including wrenches, screw drivers, and hex key.

8) Clean, silanized glass wool for particulate plugs for each sample.

9) Vials for containing the glass wool plugs after sample collection.

10) Spiking solutions and clean syringes.

11) Thermometer and hydrometer (and any other meteorological equipment desired) for evaluating the sampling conditions.

12) "Sampling Fact Sheets" and a pen.

13) This manual!!

14) Necessary boxes, trunks, tape, and packing materials for transporting the above items.

15) Any required paperwork (e.g., shipping receipt, etc.).

Once in the field, before sample collection is initiated the Ambient Air Collection System should have its sampling flow rate measured with a calibrated bubble meter. The bubble meter may be attached to the exhaust of the Nutech Air Sampler, and the exhaust flow rate monitored whenever necessary. This exhaust flow rate can be compared to the inlet flow rate before and after sample collection. Measurement of the inlet flow rate must be taken with a "calibration" tube tray attached to the Nutech Sampler (see Figure C-29) in order to approximate the pressure drop incurred with a sorbent tube tray in this position during actual sampling and to prevent the contamination of the Nutech Sampler with surfactants. This tube tray should be quickly leak-checked as described below. With the flow needle valve fully opened and the Nutech Sampler plugged into an AC power source, the Nutech Air Sampler should be turned "on" by first switching the AC switch and then the DC switch to their "up" positions. The flow needle valve is adjusted to obtain the flow rate specified by the sampling plan. The flow at the inlet of the "calibration" tube tray should be measured with the bubble meter at least three times. This should be compared with exhaust and the rotameter flow rates, and all flow rate values recorded. This procedure re-checks the calibration of the rotameter which can be used during actual sampling, in conjunction with exhaust flow rate determinations, to determine the approximate sampling flow rate and to detect any major changes in this flow rate during sample collection. This value can be used to determine a sample volume that can be compared to the volume measured by the dry gas meter. Other conditions of the Nutech Air Sampler, such as temperature and measured pressure drop, should be recorded during its "calibration" for comparison with these conditions measured during sample collection.

With a tube tray attached to the Nutech Air Sampler, a leak check must be performed to assure that air is being drawn only through the tray inlet. Since air is being drawn, not pushed, through the sorbent tubes and various connectors during sampling or calibration, a vacuum is created at any leak within the system. Therefore, this system cannot be effectively leak-checked with a leak-detection liquid because that liquid would be drawn into the sampling system at the point of any leaks and contaminate that system. However, the vacuum phenomenon can be successfully used to perform a "mechanical" leak check. This is done by first attaching the pump/tray connector to the Nutech Air Sampler with the end to be attached to the tube tray still capped. With a bubble meter attached to the exhaust of the Nutech Air Sampler, the system should be turned "on". The connector and pump should be quickly evacuated and no flow observed if no leaks are present within the system. If flow is observed, tighten all fittings until none is evident. Check internal connections within the Nutech Air ampler, if necessary. The Nutech Air Sampler should be quickly turned "off" after a leak free system is obtained. The pump/tray connector is then attached to the tube tray ("calibration" or sample) outlet, with its inlet still capped (see Figure C-30). The above procedure is then repeated. If all connections were made securely when the tube tray was assembled, a relatively leak-free system should result. If a flow rate of less than 5 mL/min is observed, then the leak-check should be considered "acceptable". A flow of 5 mL/min through small leaks is insignificant compared to the sampling flow rate of 1 or 2 L/min. The results of the leak check should be recorded and the pump turned "off" prior to opening the tube tray inlet.

After calibrating the flow rate of the Ambient Air Collection System, the final preparation should be made for sample collection with the Nutech Air Sampler turned "off", the "calibration" tube tray should be removed from the pump/tray connector and replaced with a sorbent tube tray, "loaded" with four sorbent tubes according to the procedures described previously. Care should be taken to

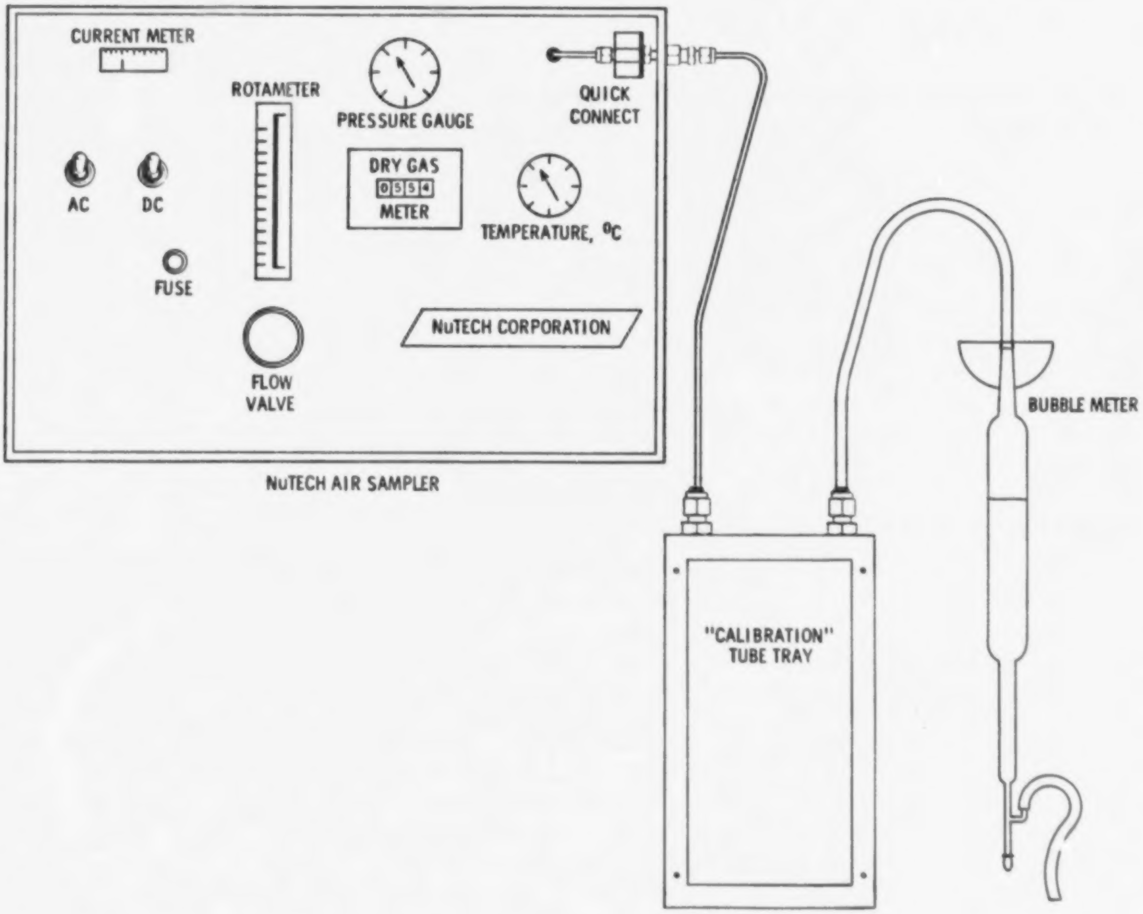
CURRENT METER
ROTAMETER
PRESSURE GAUGE
QUICK CONNECT
AC
DC
DRY GAS
0554
METER
TEMPERATURE, °C
FUSE
NuTECH CORPORATION
FLOW VALVE
BUBBLE METER
NuTECH AIR SAMPLER
"CALIBRATION" TUBE TRAY

Figure C-29. "Calibration" tube tray attached to Nutech Air Sampler and bubble meter.

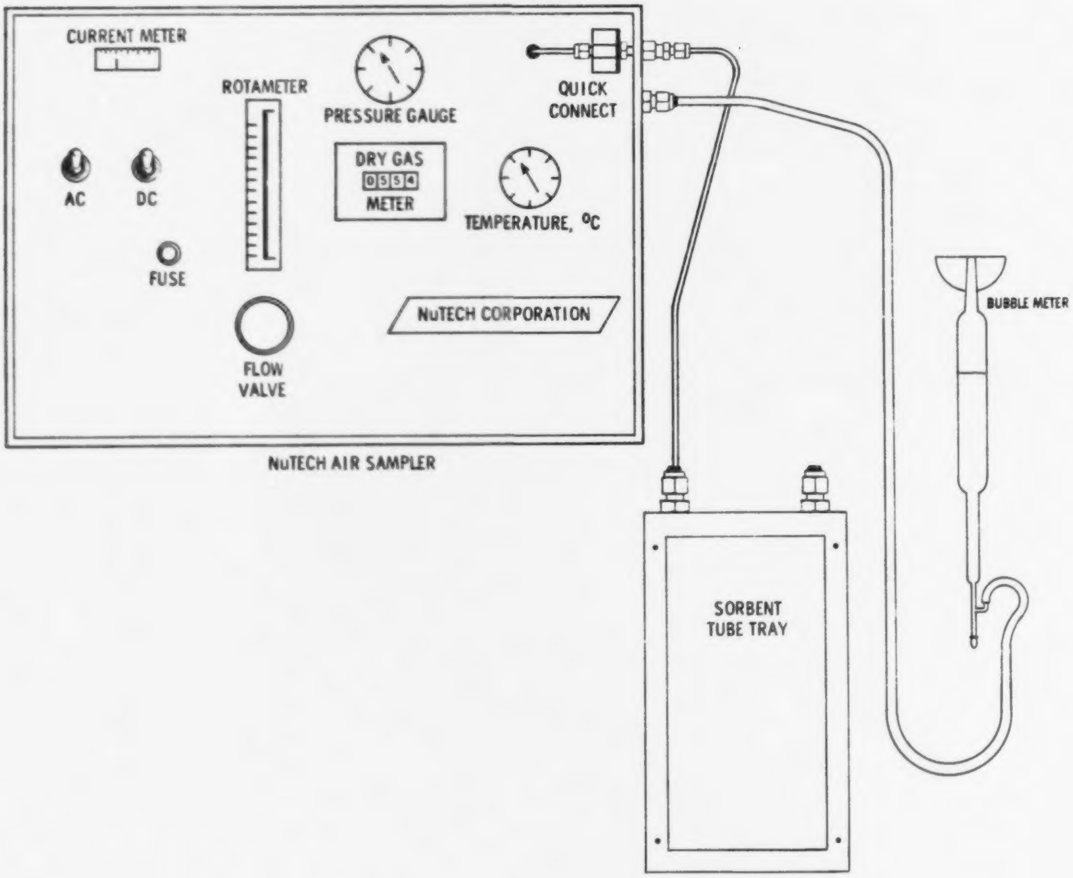
CURRENT METER
ROTAMETER
PRESSURE GAUGE
QUICK CONNECT
AC
DC
DRY GAS
0554
METER
TEMPERATURE, °C
FUSE
NuTECH CORPORATION
FLOW VALVE
NuTECH AIR SAMPLER
BUBBLE METER
SORBENT TUBE TRAY

Figure C-30. Ambient air collection system ready for sample collection.

assure that all connections are secure by leak-checking the sampling system by the above procedure.

Now the Ambient Air Collection System is ready for sample collection. First, the sampler should be placed in an appropriate location, such that the sorbent tube tray is not exposed to the exhaust of the Nutech Air Sampler. Next, the inlet plug of the tube tray should be removed and a small amount of glass wool inserted in this inlet to serve as a particulate filter. After recording the initial volume of the dry gas meter, the ambient air sampler should be turned "on" by switching first the AC switch, then the DC switch to their "up" positions. The time of sample initiation and all conditions of the Nutech Air Sampler should be recorded. Approximately every other hour after sampling is initiated, the conditions of the Nutech Air Sampler should again be recorded. Exhaust flow rates should be determined at least every other hour. This will allow the approximate flow rate to be averaged over the sampling time to obtain a sample volume which can be compared to the sample volume measured by the dry gas meter. The only other disturbance to the sampling system during sample collection, should be sample spiking, if required for the sample by the sampling plan. Both the techniques of sample spiking and the development of a sampling plan will be discussed later in this manual.

After sampling is complete (i.e., after 8 hrs.), the Nutech Air Sampler should be switched "off" and the final volume of the dry gas meter recorded. Then the glass wool plug should be removed from the sorbent tube tray inlet and stored in a glass vial. The tray inlet should be plugged, the system quickly leak-checked, and the results recorded. The pump/tray connector should be removed from the sorbent tube tray, and the outlet of the tube tray plugged. The sorbent tube tray should be disassembled in the opposite manner of assembly with the sorbent tubes removed, capped, and placed in their appropriate culture tubes. Again, this should be done as quickly as possible to prevent additional sorbent contamination and to prevent loss of sample due to diffusion.

The flow rate through the Nutech Air Sampler should again be checked after sampling and after securing the sorbent tubes. This should be done by reconnecting the "calibration" tube tray to the Nutech Air Sampler, quickly leak-checking and determining the flow rate at the "calibration" tray inlet as previously described. This should be determined with at least three trials, and all flow rates (inlet, exhaust, and rotameter) and conditions recorded. This will allow a direct comparison to the conditions originally determined prior to sample collection.

Quality Control Considerations

In order to assure that data obtained from sorbent samples are reasonable and valid, various aspects of quality control/quality assurance (QC/QA) must be maintained. One aspect of QC/QA which should be addressed is the demonstration that the laboratory, which will be performing the sampling and analyses of sorbent samples, is competent and follows accepted good laboratory practices. (A more extensive discussion of quality control procedures and considerations is presented in a special MRC-EASC publication [133].) To meet the demands for QC/QA of samples for numerous environmental and industrial hygiene programs, such a laboratory should develop and continuously improve a good laboratory practice program.

Another aspect of QC/QA involves testing the sorbent sampling/analytical method presented by various quality control measures. This should be done to practically demonstrate the validity of the method and of the samples. These control measures include evaluating standards, blanks, replicate, splits, backups, and spikes. Standard solutions of mixtures of compounds of interest (to this project) or other compounds for instrument evaluation/calibration should be analyzed to allow quantitation of compounds present in samples to generate calibration curves, to check detector linearity, and to assure that the analytical instrument and method are functioning properly. "Blanks" are sorbent tubes that are treated in a manner identical to that used for the sorbent tubes on which samples are collected except that no sample is drawn. Such "blanks" can indicate problems with contamination (e.g., from transport) and/or sorbent degradation. By collecting multiple samples on a number of tubes under identical conditions, replicate samples are collected which can provide data for determining the precision of the sampling/analytical method. When thermally desorbing the sorbent tubes for analysis, the tube effluent can be split and recollected for subsequent analyses using the same or different analytical method. Such split samples can be used to verify analytical precision or to validate analytical results by analyzing them under different conditions or using columns with different liquid phases. To evaluate the overall sampling/analytical method, backup sorbent tubes, and laboratory and field spikes are analyzed. A backup sorbent tube (Ambersorb XE-340) is placed in the fourth position during sampling to collect compounds "breaking through" the first three sorbent tubes. The compounds analyzed on this backup tube are, therefore, the compounds which were not quantitatively retained by the three sorbent system. A spike is a sorbent tube with a known quantity of the compound(s) of interest loaded on it. If the loading is done in a laboratory after sample collection or on a "blank" sorbent tube, that tube is called a "laboratory" spike. If the loading is done before or during sample collection, that tube is termed a "field" spike. Laboratory spikes can indicate sample stability and lifetime to some extent, but they are mainly used to determine desorption-efficiencies. Whether or not the compound of interests is altered during sampling or lost for another reason should be indicated by the recoveries obtained for field spikes.

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[133] W.M. Haynes, D.M. Haile, D. H. Toy, and W.M. Mess, "Guide to Good Laboratory Practices", the Environmental Analytical Sciences Center, MRC, Dayton, Ohio, March 1979.

There are numerous procedures by which laboratory and field spikes can be produced. One technique is to simply "inject" a small quantity of an analytical standard solution into the "inlet" end of a sorbent tube or the inlet of a tube tray. Although this technique is very simple and cost-effective, problems can arise due to the solvent interfering with the analyses or changing the sorbent retention characteristics. Another technique is to generate a vaporous standard mixture and "load" a small amount of this mixture into the "inlet" end of a sorbent tube. Usually this spiking technique requires special equipment (see Appendix B) that is more easily operated in a laboratory. Under these conditions all spikes must be performed prior to field sampling. Whatever technique is used should be quickly evaluated in the laboratory prior to preparing a field sampling trip.

For this project each air sample is collected in a sorbent tube tray containing three or four sorbent tubes. The analysis times for these sorbent tubes ranges from 1 to 3 hours. depending upon the sorbent type, the amount of material adsorbed, and the analytical technique. Therefore, there is a great deal of time and cost involved in the analysis of each air sample. An extensive quality control program, using a large number of sample replicates, spikes, splits, etc., would be extremely costly and, therefore, impractical. However, at least some quality control samples need to be collected and analyzed in order to demonstrate the validity of sample data, even if not enough are collected to specify the accuracy and precision of the sampling/analytical method. The best approach is to devise a sampling plan specifically designed for a particular sampling program, such that there are at least one set of blanks, a few splits, spikes, backups, replicates, and calibration/quantitation standards.

The sampling plan which is devised for a field sampling program should describe the following information for each sorbent tube:

- Tube number and sorbent type.
- Purpose of the sorbent tube (blank, sample, replicate sample, lab transport spike, sample spike, field transport spikes, backup, etc.).
- The position of the tubes in a tube tray (if any).
- The sampling conditions (if any), including date, time, sample volume and flow rate.
- The pump and pump conditions, if sampling is done.

- Any additional, pertinent information, such as the identity and amount of spikes, as well as method and time of spiking, or additional tube purpose.

An example of such a sampling plan is given in Table C-4. The information given in this table should also be marked on the outside of each of the sorbents' culture tubes to prevent switching of sorbent tubes. Grouping tubes together according to purpose during packaging will also help to keep the sorbent tubes from getting mixed-up.

Storage, Transportation, and Contamination

This part of this manual briefly reviews and summarizes information on sorbent tube storage, transportation, and protection from extraneous contamination given previously in a number of different sections. Generally, there are five phases in using sorbent tubes to collect ambient air samples. The first phase is the preparation of the sorbent tubes for sample collection, including preparation of some sorbent tubes as quality control samples; second is the protective storage and packaging of the sorbent tubes, grouped according to the sampling scheme, for safe and rapid transport to the field sampling location; third is the collection of air samples at the field location, including preparation of additional quality control samples; fourth is the protective storage and packaging of the sorbent tubes for safe and rapid transport back to the laboratory for analysis; and fifth is the analysis of the field and quality control samples. At each stage of preparation, storage, and transport, the sorbent tubes need to be protected from contamination and other adverse phenomena (e.g., breakage, sunlight, excessive heat, etc.) which could affect the materials adsorbed on the tubes and, hence, the validity of their data.

In review, to prevent the contamination of the sorbent tubes with extraneous materials during their preparation, the following guidelines should be observed.

1) All glassware and other hardware materials used during sorbent tube preparation should be meticulously cleaned prior to preparing the sorbent tubes.

2) Hardware and other materials which will be used to prepare the sorbent tubes should never be handled with bare hands. Protective gloves and/or clean utensils should be used to handle these materials.

3) Ultra-high purity solvents should be used during the soxhlet extraction of sorbent materials and teflon tape on sleeves (not silicone grease) should be used to seal the glass joints of the extraction glassware.

TABLE C-4. FIELD SAMPLING PLAN

Tube #	Sorbent type	Purpose	Tray position	Sampling Date	Sampling Times	Sampling Volume	Sampling Flow rate	Other information
40	Tenax	Sample #1	1	4/14	~8AM-~4PM	~1100 L	~2.3 L/min.	
50	Porapak R	Sample #1	2					
63	Ambersorb	Sample #1	3					
60	Ambersorb	Backup-Sample #1	4					
43	Tenax	Blank	-	-	-	-	-	
46	Porapak R	Blank	-	-	-	-	-	
56	Ambersorb	Blank	-	-	-	-	-	
38	Tenax	Calibration	1	4/14 & 4/15	-	-	~2.3 L/min	
55	Porapak R	Calibration	2					
61	Ambersorb	Calibration	3					
58	Ambersorb	Calibration	4					
36	Tenax	Transport spike	-	-	-	-	-	Lab spike, method A spike #2, spiked @ 11:30 AM, 4/11/80
52	Porapak R	Transport spike	-	-	-	-	-	
65	Ambersorb	Transport spike	-	-	-	-	-	
41	Tenax	Sample #4 - spike	1	4/15	~8AM-~4PM	~1100 L	~2.3 L/min	Field spike, method B spike #2, spike 15 min after starting sampling
49	Porapak R	Sample #4 - spike	2					
62	Ambersorb	Sample #4 - spike	3					
57	Ambersorb	Backup-sample #4 spike	4					
39	Tenax	Transport spike	-	-	-	-	-	Field spike, method A spike #2, spike ~3:00 PM 4/14/80
47	Porapak R	Transport spike	-	-	-	-	-	
59	Ambersorb	Transport spike	-	-	-	-	-	
37	Tenax	Xtra - "Blank"	-	-	-	-	-	To replace any other tubes broken (except lab transport spikes)
45	Tenax	Xtra - "Blank"	-	-	-	-	-	
51	Porapak R	Xtra - "Blank"	-	-	-	-	-	
48	Porapak R	Xtra - "Blank"	-	-	-	-	-	
64	Ambersorb	Xtra - "Blank"	-	-	-	-	-	
66	Ambersorb	Xtra - "Blank"	-	-	-	-	-	

4) A charcoal trap should be used in the vacuum line of a vacuum oven during the vacuum drying of the sorbent materials.

5) The environment to which the sorbent materials, or tubes are exposed should be as clean and dry as possible.

6) During the thermal conditioning of the sorbent tubes, the gas stream should be pre-purified by passing it through a drying trap and a charcoal trap.

7) After thermal conditioning, the sorbent tubes should be quickly capped and stored.

8) If a sorbent tube is to be spiked, the spiking solution or vaporous mixture should be carefully and "freshly" prepared, the spiking materials meticulously cleaned, and the spiking performed as quickly as possible.

After preparation, the sorbent tubes should be stored tightly capped with metal fixings and viton o-rings, and contained within culture tubes. They should be used to collect air samples within one week after thermal conditioning. This insures sorbent background is at a minimal level during sample collection. In addition, all the sorbent tubes, stored the same way as described above, should then be analyzed at least within one month, preferably within two weeks, after sample collection. While being stored or transported the capped and contained sorbent tubes should be kept in an environment as clean and dry as is practical. Furthermore, they should not be exposed to excessively hot temperatures, which would induce sorbent degradation and/or in-situ sample reactions, or to excessively cold temperatures, which could cause a change in sorbent properties and/or condense water out of the collected samples. A cool environment, at approximately ambient temperatures (15°C to 25°C), would be preferable. The sorbent tubes should also be protected from light, especially sunlight, during storage and transport to prevent light-induced reactions or degradations. To help protect the sorbent tubes from breakage during transport, clean glass wool can be wrapped around the sorbent tubes within the culture tubes. These culture tubes can be labeled and grouped according to the field sampling plan, and packaged with protective packing materials (e.g., styrofoam, bubble-sheets, etc.) inside a box or small suitcase. Finally, all paperwork associated with the transport of the sorbent tubes, sampling systems, and associated supplied should be prepared in advance of a field sampling trip.

During sample collection, certain guidelines, which are similar to the ones described for sorbent tube preparation, should be followed to prevent the contamination of the sorbent tubes with extraneous materials. These guidlines are listed below.

1) All hardware materials used during sample collection should be meticulously cleaned prior to field sampling.

2) Protective gloves and/or clean utensils should be used when handling the sorbent tubes during field sampling. Furthermore, extra care should be taken not to touch or otherwise contaminate the sorbent tube ends.

3) The sorbent tube tray should be assembled quickly, with the sorbent tubes exposed to the atmosphere as little as possible.

4) All fittings should be securely tightened with wrenches. They should be leak-checked according to the procedure previoUsly described, not with a leak-detection fluid since this can contaminate the sorbent tubes.

5) If a sorbent tube is to be spiked, with a spiking solution, the solution should be carefully and "freshly" prepared, the spiking materials meticulously cleaned, and the spiking performed as quickly as possible.

6) The tube tray lid should be on the tube tray during sampling to protect the sorbent tubes from sunlight.

7) If possible, the sorbent tube tray should be kept out of "hot" locations during sampling. For example, sampling should be done in a shaded location rather than on asphalt or concrete in hot, direct sunlight.

8) Sampling should be performed in a location away from sources of atmospheric contamination (e.g., cigarette smoke, fumes from automobile and truck exhausts, flowers, etc.), if they are not of interest.

Records

As mentioned numerous times in this manual, it is necessary to keep accurate, detailed records of all aspects of sorbent sampling. These records should include information on the history of each sorbent tube, the sampling schemes for each sampling program, all sampling conditions and flow rates, the sorbent tube storage and transportation conditions, the log in and transfer of samples, and the analytical methods, conditions, and results. All of these records help to insure the accuracy of the final results obtained and/or to identify the cause of any problems or discrepancies observed during sampling or in the analytical results.

The purpose of keeping histories for each sorbent tube is to allow the quick review of how and when the tube was prepared, and how, when, and what types of samples to which the sorbent tube was exposed after preparation. This allows variations in sampling results to be traced to variations in the histories of the sorbent tubes used in a particular sampling program. Furthermore, accurate histories help to prevent sorbent tubes from getting "mixed-up", from being stored for unreasonably long periods of time (e.g., 5 years), or from being used an unreasonable number of times (e.g., 1000 times) for collecting samples. The information that should be recorded in a sorbent log-book while preparing sorbent tubes was given previously Figure C-5, in this manual. Such records should be kept for each sorbent tube. In addition, information such as shown in Figure C-31 should also be recorded in the sorbent log book for each sorbent tube each time it is used to collect a sample. Although not all the information shown may be available for all tubes and all samples, the sorbent log book should be kept as complete as possible.

For field sampling, record-keeping begins with the development of a sampling plan, as discussed previously. This sampling plan is used as a master scheme to coordinate sampling and sampling information. Information on all sampling conditions, including weather, flow rate, and sorbent cartridges, should be recorded on a sampling fact sheet for each sample specified in the sampling plan. An example of such a sampling fact sheet which should be completed when collecting a sample with the ambient air collection system is depicted in Figure C-32. A fact sheet should also be completed for each set of quality control samples. Keeping such detailed information during a field sampling program can help to define problems with the sampling technique and/or method. Information is also recorded in the fact sheets regarding sorbent tube storage, transportation, and transfer for analysis.
Once field sampling is completed and the sorbent tubes are received at a laboratory for analysis, these samples should be logged in through the laboratory's sample log-in system for proper transfer to analytical personnel. As part of that laboratory's quality control/quality assurance program, this sample log-in system should allow the easy review of the chain-of-custody (record of individual(s) charged with responsibility for these samples) of a set of samples and ready coordination of sorbent tube preparation, field sampling, and analytical information and reports.

Reconditioning Sorbent Cartridges

After collecting and analyzing a set of ambient air samples, the sorbent tubes can be reconditioned for subsequent sampling programs. This reconditioning can be done in one of two ways. The first method is simply to thermally condition the sorbent tubes as described in previously for the original preparation of these cartridges for sampling. This should be done soon after the sorbent air samples are analyzed in order to remove, as quickly as possible, any compounds from the sorbent tubes not removed during these analyses. This helps to insure that any compounds of the air sample still remaining on the sorbent tubes will not irreversibly adsorb on or cause the degradation of the sorbent materials. However,

"Sampling Lifetime"

Name:

Tube #: Sorbent Type: Date Packed:
Last Conditioning Procedure:
Date:
Storage Procedure:
Storage Dates:
Transportation Procedure:
Packaging Procedure:
Lab to Field Dates: Field to Lab Dates:

Sampling Conditions

Sampling Date: Sampling Fact Sheet #:
Type of Sample: Lab Blank Field Blank Lab Spike
Backup Transport Spike Field Sample Spike
Field Sample
Log In Date: Log In #:
Analysis Request #: Analysis Request Date:
Analysis Procedure:

Analysis Dates Name:
Analytical Results (briefly):

Analytical Results Reference (NB. Pg. or Report #):

Date Sample Log Closed:

Sorbent Cartridge Fate

Storage Procedure: Dates:
Reconditioning Procedure:
Reconditioning Date:
Log Book Reference Pg:

Date Sorbent Tube Unpacked: Comment:

Recycled? Sorbent: Glass Cartridge:
Log Book Pg:

Figure C-31. Information which should be recorded in a sorbent logbook.

AMBIENT AIR COLLECTION SYSTEM:

SAMPLING FACT SHEET #__

Date of Sampling: Name(s):

Location (City, State, Street, Etc.):

Atmospheric Conditions:

TYPE OF SAMPLE Lab Blank Field Blank Lab Spike
Transport Spike Field Sample Spike Field Sample Sample Backup
Spike Backup Calibration

SORBENT CARTRIDGES

Tube #	Sorbent Type	Condition of Cartridge	Tray Position	Comments

IF SPIKE: Date Spiked: Notebook Page:

Procedure:

Amounts & Names of Compounds:

PUMP CONDITIONS Power: AC DC No. of Valve Turns:

Date of Last Dry Gas Meter Calibration:

Initial Time: Final Time:

Initial Dry Gas Volume: Final Dry Gas Volume:

Figure C-32. Sampling fact sheet.

Flow Rate Observed for System Calibration and Sample Monitoring

		Time for mL of flow, min			Ave. Flow Rate, mL/min	Rotameter Reading, L/min	Pressure Gauge, in H_2O	Power Gauge, Amps	Temperature, °C	Dry Gas Meter, m^3
Setup	Time	Trial 1	Trial 2	Trial 3						

Figure C-32. (continued)

EVALUATION OF FLOW MEASUREMENTS

Location of Flow Measurement	Flow Rates mL/min			Sampling Time, min	Estimated Sample Volume, liters		
	Hi	Ave.	Lo		Hi	Ave.	Lo

TRANSPORTATION AND STORAGE

Storage Procedures/Conditions:

Transportation Procedures/Conditions:

Packaging Procedures/Conditions:

Lab to Field Dates: Field to Lab Dates:

SAMPLE TRANSFER

Log-In Date: Log-In #(s):

Analysis Request #: Analysis Request Date:

Requestor: Sent to:

Figure C-32 (continued)

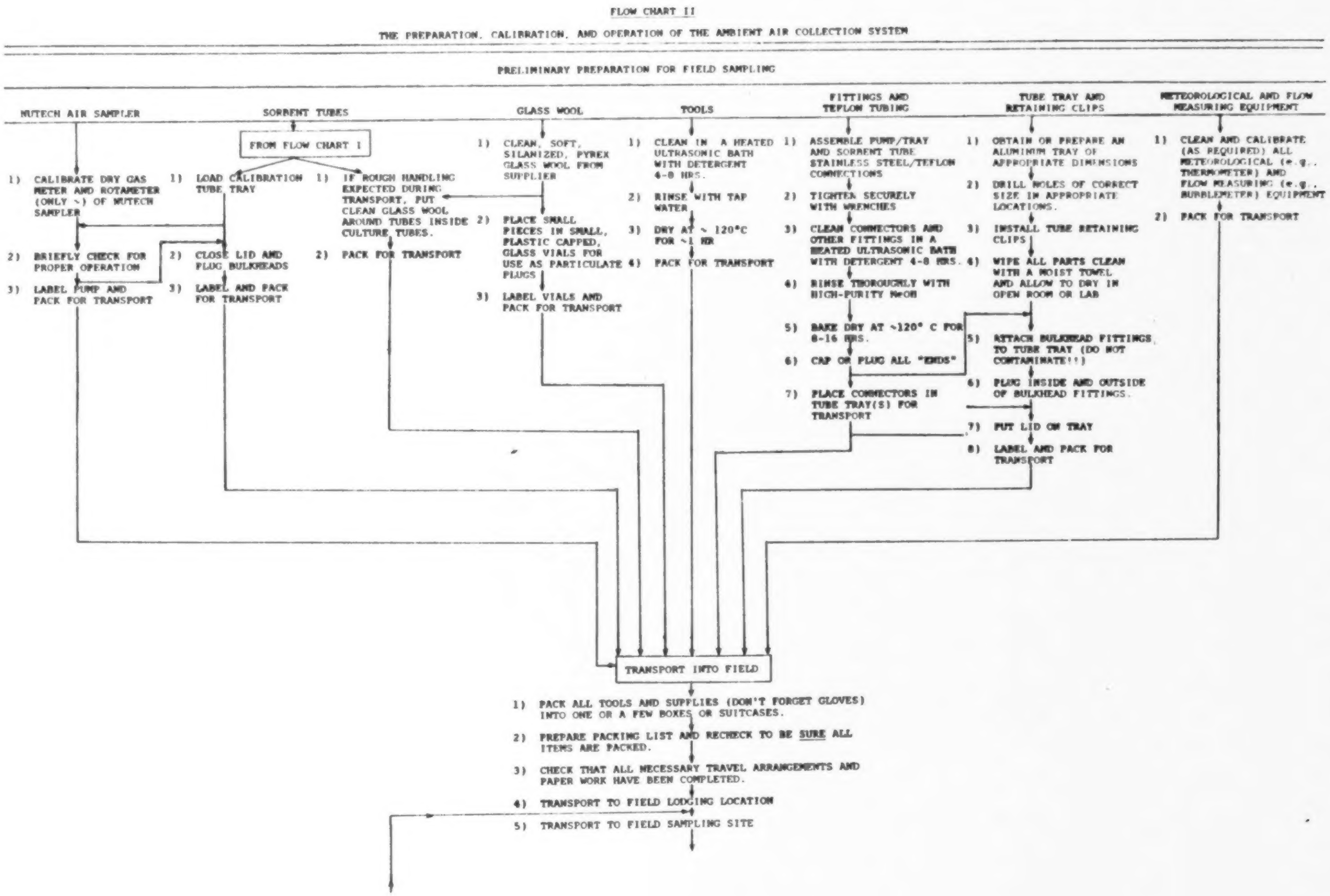
after the sorbent tubes are thermally reconditioned, a set of blanks should be analyzed to determine if the background of the sorbent tubes is "acceptable". To be "acceptable", these backgrounds should be the same types and levels as determined for the first air sample quality control blanks. If the reconditioned sorbent tubes are found to be "acceptable", they should be used for collecting another set of air samples within one week of being thermally conditioned, or be thermally conditioned again immediately prior to the next sampling program.

If the sorbent tube backgrounds are found to be unacceptable, or if these tubes have been used to collect a number of air samples (~5), then a second, more rigorous, reconditioning method should be used to rejuvenate the sorbent materials. By this method, after the sorbent tube air samples have been analyzed, the sorbent tubes should be "unpacked". The glass wool plugs retaining the sorbent materials within the sorbent tubes should be removed and discarded. The sorbent materials should be "poured" into clean glass jars, keeping the different sorbent materials separate. The sorbent materials should be sieved (60 mesh for Tenax and Ambersorb, 80 mesh for Porapak R) to remove fine particles. Then the sorbents should undergo the extraction/drying procedures given previously for cleaning "new" sorbent materials. After cleaning and re-deactivating the glass cartridges (now empty) by the method given previously (discarding and replacing cartridges with badly broken ends), the sorbent materials are then "repacked" in the glass cartridges. These "re-packed" sorbent tubes should receive a new page in the sorbent log-book, with reference back to the original sorbent tubes, and should be indicated as "second generation" sorbent tubes. Within one week of the next sampling program these sorbent tubes should be thermally conditioned. The hardware materials for the storage of these sorbent tubes should also be re-cleaned according to the procedures given previously. (Hardware used within the sorbent tube tray or for connecting the pump and tube tray should be re-cleaned between each sampling program.)

Since each sorbent tube has a definite "lifetime" after which its capacity for retaining compounds diminishes or its background level becomes excessively high, limits must be placed on the number of times a sorbent can be used. For this project, a sorbent tube (with "acceptable" background) may be used to collect up to five air samples or be thermally conditioned up to fifteen times (whichever comes first), before being re-extracted or discarded. The sorbent materials may be re-extracted twice (i.e., three sorbent tube "generations") for rejuvenating these materials. This allows a total up to fifteen air samples, forty-five thermal conditionings, and three extractions for a lot of sorbent material.

Flow Chart II

The flow chart given in Figure C-33 summarizes the procedure for preparing the Ambient Air System, for collecting air samples, and for reconditioning sorbent tubes.



FLOW CHART II

THE PREPARATION, CALIBRATION, AND OPERATION OF THE AMBIENT AIR COLLECTION SYSTEM

PRELIMINARY PREPARATION FOR FIELD SAMPLING

NUTECH AIR SAMPLER
1) CALIBRATE DRY GAS METER AND ROTAMETER (ONLY ~) OF NUTECH SAMPLER
2) BRIEFLY CHECK FOR PROPER OPERATION
3) LABEL PUMP AND PACK FOR TRANSPORT

SORBENT TUBES
FROM FLOW CHART I
1) LOAD CALIBRATION TUBE TRAY
2) CLOSE LID AND PLUG BULKHEADS
3) LABEL AND PACK FOR TRANSPORT

1) IF ROUGH HANDLING EXPECTED DURING TRANSPORT, PUT CLEAN GLASS WOOL AROUND TUBES INSIDE CULTURE TUBES.
2) PACK FOR TRANSPORT

GLASS WOOL
1) CLEAN, SOFT, SILANIZED, PYREX GLASS WOOL FROM SUPPLIER
2) PLACE SMALL PIECES IN SMALL, PLASTIC CAPPED, GLASS VIALS FOR USE AS PARTICULATE PLUGS
3) LABEL VIALS AND PACK FOR TRANSPORT

TOOLS
1) CLEAN IN A HEATED ULTRASONIC BATH WITH DETERGENT 4-8 HRS.
2) RINSE WITH TAP WATER
3) DRY AT ~ 120°C FOR ~1 HR
4) PACK FOR TRANSPORT

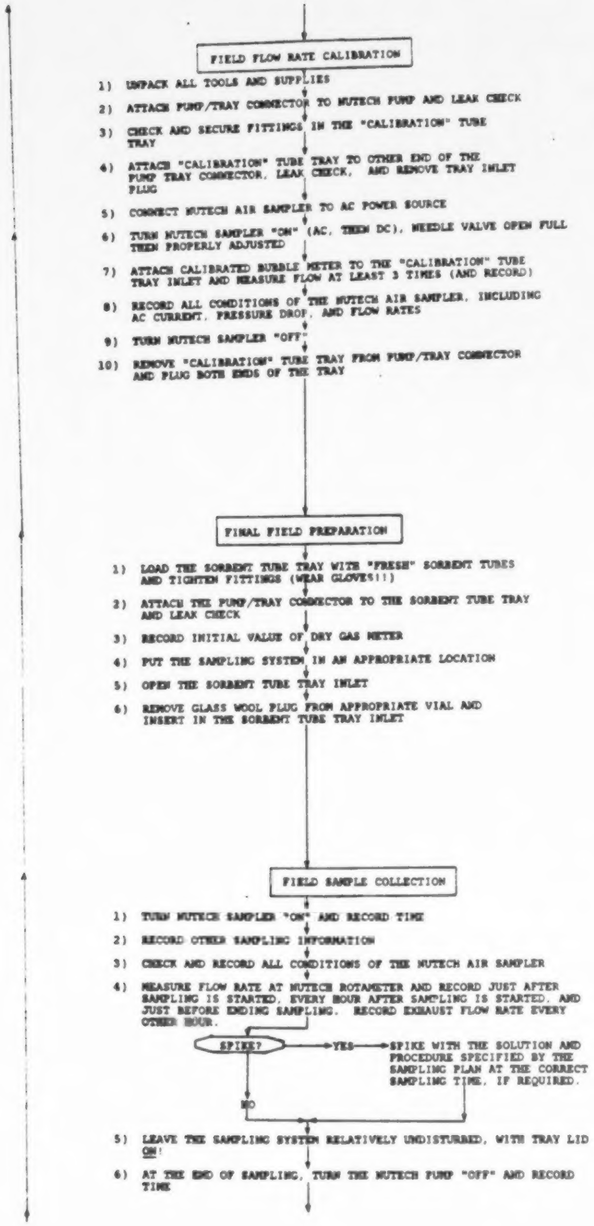
FITTINGS AND TEFLON TUBING
1) ASSEMBLE PUMP/TRAY AND SORBENT TUBE STAINLESS STEEL/TEFLON CONNECTIONS
2) TIGHTEN SECURELY WITH WRENCHES
3) CLEAN CONNECTORS AND OTHER FITTINGS IN A HEATED ULTRASONIC BATH WITH DETERGENT 4-8 HRS.
4) RINSE THOROUGHLY WITH HIGH-PURITY MeOH
5) BAKE DRY AT ~120° C FOR 8-16 HRS.
6) CAP OR PLUG ALL "ENDS"
7) PLACE CONNECTORS IN TUBE TRAY(S) FOR TRANSPORT

TUBE TRAY AND RETAINING CLIPS
1) OBTAIN OR PREPARE AN ALUMINUM TRAY OF APPROPRIATE DIMENSIONS
2) DRILL HOLES OF CORRECT SIZE IN APPROPRIATE LOCATIONS.
3) INSTALL TUBE RETAINING CLIPS
4) WIPE ALL PARTS CLEAN WITH A MOIST TOWEL AND ALLOW TO DRY IN OPEN ROOM OR LAB
5) ATTACH BULKHEAD FITTINGS, TO TUBE TRAY (DO NOT CONTAMINATE!!)
6) PLUG INSIDE AND OUTSIDE OF BULKHEAD FITTINGS.
7) PUT LID ON TRAY
8) LABEL AND PACK FOR TRANSPORT

METEOROLOGICAL AND FLOW MEASURING EQUIPMENT
1) CLEAN AND CALIBRATE (AS REQUIRED) ALL METEOROLOGICAL (e.g., THERMOMETER) AND FLOW MEASURING (e.g., BUBBLEMETER) EQUIPMENT
2) PACK FOR TRANSPORT

TRANSPORT INTO FIELD
1) PACK ALL TOOLS AND SUPPLIES (DON'T FORGET GLOVES) INTO ONE OR A FEW BOXES OR SUITCASES.
2) PREPARE PACKING LIST AND RECHECK TO BE SURE ALL ITEMS ARE PACKED.
3) CHECK THAT ALL NECESSARY TRAVEL ARRANGEMENTS AND PAPER WORK HAVE BEEN COMPLETED.
4) TRANSPORT TO FIELD LODGING LOCATION
5) TRANSPORT TO FIELD SAMPLING SITE

Figure C-33. Flow Chart II.



FIELD FLOW RATE CALIBRATION

1) UNPACK ALL TOOLS AND SUPPLIES
2) ATTACH PUMP/TRAY CONNECTOR TO NUTECH PUMP AND LEAK CHECK
3) CHECK AND SECURE FITTINGS IN THE "CALIBRATION" TUBE TRAY
4) ATTACH "CALIBRATION" TUBE TRAY TO OTHER END OF THE PUMP TRAY CONNECTOR, LEAK CHECK, AND REMOVE TRAY INLET PLUG
5) CONNECT NUTECH AIR SAMPLER TO AC POWER SOURCE
6) TURN NUTECH SAMPLER "ON" (AC, THEN DC), NEEDLE VALVE OPEN FULL THEN PROPERLY ADJUSTED
7) ATTACH CALIBRATED BUBBLE METER TO THE "CALIBRATION" TUBE TRAY INLET AND MEASURE FLOW AT LEAST 3 TIMES (AND RECORD)
8) RECORD ALL CONDITIONS OF THE NUTECH AIR SAMPLER, INCLUDING AC CURRENT, PRESSURE DROP, AND FLOW RATES
9) TURN NUTECH SAMPLER "OFF"
10) REMOVE "CALIBRATION" TUBE TRAY FROM PUMP/TRAY CONNECTOR AND PLUG BOTH ENDS OF THE TRAY

FINAL FIELD PREPARATION

1) LOAD THE SORBENT TUBE TRAY WITH "FRESH" SORBENT TUBES AND TIGHTEN FITTINGS (WEAR GLOVES!!)
2) ATTACH THE PUMP/TRAY CONNECTOR TO THE SORBENT TUBE TRAY AND LEAK CHECK
3) RECORD INITIAL VALUE OF DRY GAS METER
4) PUT THE SAMPLING SYSTEM IN AN APPROPRIATE LOCATION
5) OPEN THE SORBENT TUBE TRAY INLET
6) REMOVE GLASS WOOL PLUG FROM APPROPRIATE VIAL AND INSERT IN THE SORBENT TUBE TRAY INLET

FIELD SAMPLE COLLECTION

1) TURN NUTECH SAMPLER "ON" AND RECORD TIME
2) RECORD OTHER SAMPLING INFORMATION
3) CHECK AND RECORD ALL CONDITIONS OF THE NUTECH AIR SAMPLER
4) MEASURE FLOW RATE AT NUTECH ROTAMETER AND RECORD JUST AFTER SAMPLING IS STARTED, EVERY HOUR AFTER SAMPLING IS STARTED, AND JUST BEFORE ENDING SAMPLING. RECORD EXHAUST FLOW RATE EVERY OTHER HOUR.

SPIKE WITH THE SOLUTION AND PROCEDURE SPECIFIED BY THE SAMPLING PLAN AT THE CORRECT SAMPLING TIME, IF REQUIRED.

5) LEAVE THE SAMPLING SYSTEM RELATIVELY UNDISTURBED, WITH TRAY LID ON!
6) AT THE END OF SAMPLING, TURN THE NUTECH PUMP "OFF" AND RECORD TIME

Figure C-33. (continued)

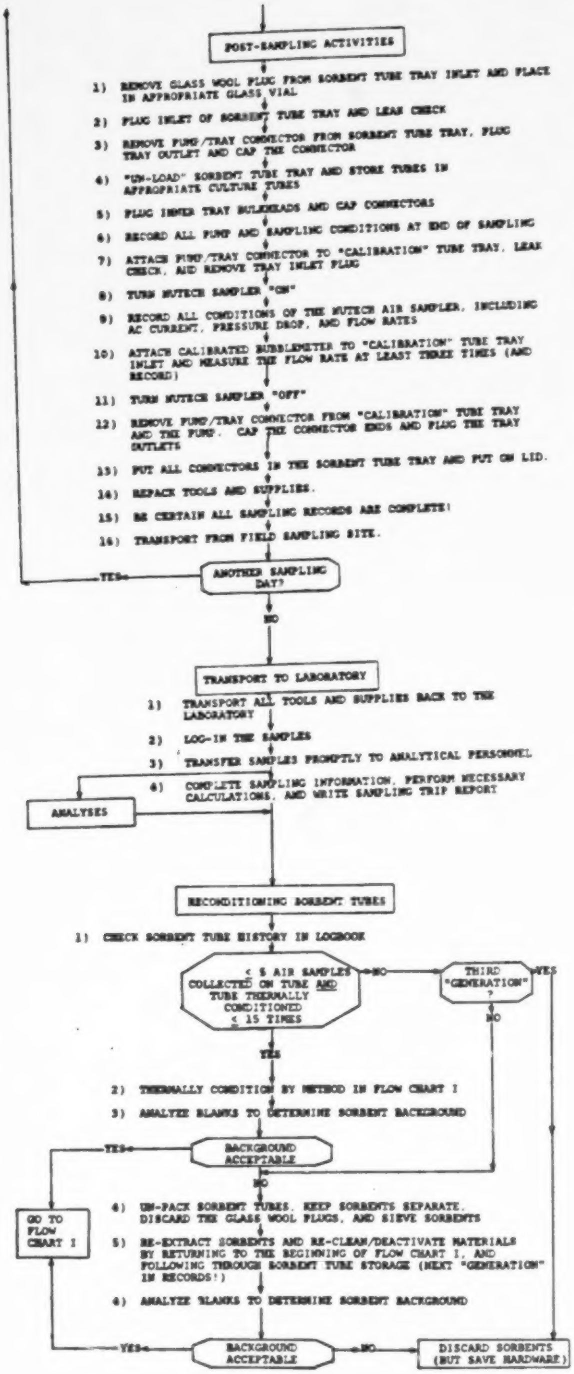

POST-SAMPLING ACTIVITIES
1) REMOVE GLASS WOOL PLUG FROM SORBENT TUBE TRAY INLET AND PLACE IN APPROPRIATE GLASS VIAL
2) PLUG INLET OF SORBENT TUBE TRAY AND LEAK CHECK
3) REMOVE PUMP/TRAY CONNECTOR FROM SORBENT TUBE TRAY, PLUG TRAY OUTLET AND CAP THE CONNECTOR
4) "UN-LOAD" SORBENT TUBE TRAY AND STORE TUBES IN APPROPRIATE CULTURE TUBES
5) PLUG INNER TRAY BULKHEADS AND CAP CONNECTORS
6) RECORD ALL PUMP AND SAMPLING CONDITIONS AT END OF SAMPLING
7) ATTACH PUMP/TRAY CONNECTOR TO "CALIBRATION" TUBE TRAY, LEAK CHECK, AND REMOVE TRAY INLET PLUG
8) TURN NUTECH SAMPLER "ON"
9) RECORD ALL CONDITIONS OF THE NUTECH AIR SAMPLER, INCLUDING AC CURRENT, PRESSURE DROP, AND FLOW RATES
10) ATTACH CALIBRATED BUBBLEMETER TO "CALIBRATION" TUBE TRAY INLET AND MEASURE THE FLOW RATE AT LEAST THREE TIMES (AND RECORD)
11) TURN NUTECH SAMPLER "OFF"
12) REMOVE PUMP/TRAY CONNECTOR FROM "CALIBRATION" TUBE TRAY AND THE PUMP. CAP THE CONNECTOR ENDS AND PLUG THE TRAY OUTLETS
13) PUT ALL CONNECTORS IN THE SORBENT TUBE TRAY AND PUT ON LID.
14) REPACK TOOLS AND SUPPLIES.
15) BE CERTAIN ALL SAMPLING RECORDS ARE COMPLETE!
16) TRANSPORT FROM FIELD SAMPLING SITE.
ANOTHER SAMPLING DAY?
YES
NO
TRANSPORT TO LABORATORY
1) TRANSPORT ALL TOOLS AND SUPPLIES BACK TO THE LABORATORY
2) LOG-IN THE SAMPLES
3) TRANSFER SAMPLES PROMPTLY TO ANALYTICAL PERSONNEL
4) COMPLETE SAMPLING INFORMATION, PERFORM NECESSARY CALCULATIONS, AND WRITE SAMPLING TRIP REPORT
ANALYSES
RECONDITIONING SORBENT TUBES
1) CHECK SORBENT TUBE HISTORY IN LOGBOOK
< 5 AIR SAMPLES COLLECTED ON TUBE AND TUBE THERMALLY CONDITIONED ≤ 15 TIMES
NO
THIRD "GENERATION" ?
YES
NO
YES
2) THERMALLY CONDITION BY METHOD IN FLOW CHART I
3) ANALYZE BLANKS TO DETERMINE SORBENT BACKGROUND
BACKGROUND ACCEPTABLE
YES
NO
GO TO FLOW CHART I
4) UN-PACK SORBENT TUBES, KEEP SORBENTS SEPARATE, DISCARD THE GLASS WOOL PLUGS, AND SIEVE SORBENTS
5) RE-EXTRACT SORBENTS AND RE-CLEAN/DEACTIVATE MATERIALS BY RETURNING TO THE BEGINNING OF FLOW CHART I, AND FOLLOWING THROUGH SORBENT TUBE STORAGE (NEXT "GENERATION" IN RECORDS!)
6) ANALYZE BLANKS TO DETERMINE SORBENT BACKGROUND
YES
BACKGROUND ACCEPTABLE
NO
DISCARD SORBENTS (BUT SAVE HARDWARE)

Figure C-33. (continued)